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OPTIMIZATION OF JP-4 FUEL EMULSIONS AND DEVELOPMENT OF DESIGN CONCEPTS FOR THEIR DEMULSIFICATION

Final Report

By

J. G. Harris

E. A. Steimetz

November 1968

**U. S. ARMY AVIATION MATERIEL LABORATORIES
FORT EUSTIS, VIRGINIA**

**CONTRACT DAAJ02-67-C-0107
MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO**

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DEPARTMENT OF THE ARMY
U. S. ARMY AVIATION MATERIEL LABORATORIES
FORT EUSTIS, VIRGINIA 23604

This report contains the results of investigations of emulsified JP-4 aviation fuel conducted by Monsanto Research Corporation, Dayton, Ohio, under the terms of Contract DAAJ02-67-C-0107.

The purpose of the program was twofold: (1) to modify the formulation of a tallow amine acetate JP-4 emulsion developed under a prior-year contract to improve its physical, chemical, and rheological properties, and (2) to investigate demulsification processes that might lend themselves to scale-up techniques suitable for application in the Army field environment.

The program objectives were met. The recommended emulsion formulation, together with demulsification systems tested, is discussed in detail herein.

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OPTIMIZATION OF JP-4 FUEL EMULSIONS AND
DEVELOPMENT OF DESIGN CONCEPTS FOR THEIR DEMULSIFICATION

Final Report

By

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Prepared by

Monsanto Research Corporation
Dayton Laboratory
Dayton, Ohio

for

U. S. ARMY AVIATION MATERIEL LABORATORIES
FORT EUSTIS, VIRGINIA

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ABSTRACT

Optimization of the Monsanto Emulsified Fuel (MEF) was accomplished following evaluation of a 168 formulation matrix. Thermal and storage stability was best when a 1% to 2% excess of acid was used to neutralize the tallow amine. Emulsion droplet size was shown to be more a function of preparation than of thermal effect or aging. Attempts at improvement of an MEF-1 formulation from the investigation by using coupling agents or corrosion inhibitors were unsuccessful. However, change in emulsifier from tallow amine to oleyl amine markedly improved thermal stability and minimized yield stress value variation at extremes of temperature. Substitution of glycolic acid for acetic acid (the MEF-2 formula) reduced mild steel corrosion to near zero proportions and reduced cuprous metal corrosion to one-third that of the MEF formula.

Evaluation of the MEF-2 formula showed that the initial viscosity decreased on storage due to loss of emulsified air and concurrently increased in density. Agitation by hand, gear, or centrifugal pump caused an increase in yield stress. Five days at 500 g's reduced the emulsifier level only 16%, and the oleyl amine glycolate was soluble in JP-4 to the extent of 0.0015-0.0018% remaining essentially in the external phase. A partial explanation for the lack of emulsion adhesion to metal surfaces is its low surface tension of about 24 dynes/cm, near that of JP-4 alone. Microbial resistance equalled that of JP-4, vapor loss was the same as that of the original MEF, and heat transfer properties were poorer than those of JP-4.

Recovery of JP-4 by breaking the emulsion by mechanical shear was possible by two general techniques: pressure drop through a small orifice or passage through orifices of micron dimensions. Maximum JP-4 recovery was 90% at laboratory rates of 10 gpm using a pressure drop orifice-vibrating reed system. Another potential system comprised passage through membranes with micron-sized perforations. Both systems require a coalescer to assure maximum removal of suspended external phase. Further attempts to improve the effective chemical demulsification system were unsuccessful. Fuel from shear demulsification is only slightly higher than specification maxima for existent and potential gum due to the soluble retained amine.

FOREWORD

This program was performed under the authorization of the U. S. Army Aviation Materiel Laboratories under Contract DAAJ02-67-C-0107, and covers the period from 29 June 1967 through 29 June 1968. A subcontractor was the Research Institute of the University of Dayton on emulsion biocidal characteristics. Several companies listed under Phase II of this report tested their equipment capability to break the fuel emulsion to recover JP-4.

The consultation and guidance given by Mr. W. J. Nolan and Captain G. W. Bowling of the Aviation Materiel Laboratories have been most helpful and appreciated.

Monsanto Research Corporation personnel who contributed to this effort were E. L. Brown, J. R. Gibson, D. L. Harris, L. E. Holboke, C. J. Huffman, M. F. Borchers, W. G. Scribner, and E. A. Steinmetz under the direction of Jay C. Harris, the project manager.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.	111
FOREWORD.	v
LIST OF ILLUSTRATIONS	xi
LIST OF TABLES.	xii
INTRODUCTION	1
DEVELOPMENT OF PROBLEM	2
EXPERIMENTAL DATA AND DISCUSSION.	4
PHASE I. MEF-1 Development	4
1. Emulsion Matrix	4
2. Matrix Emulsion Stabilities	4
3. Low-Temperature Storage Investigation.	11
4. Effect of pH and Acidity Excess.	11
5. Formulas for Storage Tests	14
5.1 Droplet Size	17
5.2 Yield Stress Values	17
6. MEF-1 Selection	18
MEF-2 Development.	20
7. Coupling Agents	20
8. Corrosion	25
8.1 Emulsion pH - Effect on Excess Tallow Amine	25
8.2 Additives	26
8.3 Replacement of Acetic Acid in the Amine Acetate	26
9. Emulsifier Improvement.	28
9.1 Surfactant 1	30
9.2 Surfactant 2	30
9.3 Surfactant 3	30

	<u>Page</u>
9.4 Oleyl Amine.	30
9.5 Technical Oleyl Amine From Various Sources	32
9.6 Oleyl Amine MEF-2 Emulsion Preparation. .	36
9.7 Cloud and Freezing Points of MEF-2 External Phase Concentrate	38
10. Emulsifier Stoichiometry	38
10.1 Mild Steel Corrosion.	38
10.2 Emulsion pH.	39
10.3 Emulsion Stability	39
11. MEF-2 Formula Selection	40
MEF-2 Properties	43
12. Yield Stress Change With Age.	43
13. Specific Gravity Change With Time	43
14. Emulsifier Solubility	46
14.1 C ¹⁴ -Labeled Glycolic Acid	47
14.2 Oleyl Amine Titration	47
15. Droplet Size Variation With Age.	49
16. Emulsifier Migration	50
16.1 Radiotracer Technique	50
16.2 Centrifugation.	51
16.3 Emulsion Appearance	54
16.4 Emulsifier Migration at 140°F.	54
17. Agitation After Aging	55
18. Thermal Conductivity	55
19. Heat Transfer Properties	58
19.1 Test Procedure	59
19.2 Test Data	59
19.3 Discussion of Results	61
20. Surface Free-Energy of Emulsion.	61
21. MEF-2 Metal Corrosion	62

	<u>Page</u>
22. Compatibility With Elastomers	66
23. Vapor Loss.	66
24. Microbial Resistance	69
25. Emulsion Preparation	70
25.1 Direct Emulsion Formulation	71
25.2 Emulsion Formulation From XPC.	71
25.3 Emulsion.	71
PHASE II. Demulsification.	72
1. General.	72
2. Preliminary Laboratory Experiments With Shear Equipment	73
2.1 Blade Blender	73
2.2 Centrifugal Pump	73
2.3 Internal Rotary Gear Pump	74
2.4 High Shear Mixer - Open System	74
2.5 High Shear Mixer - Closed System.	75
3. Investigations by Equipment Manufacturers	75
4. Laboratory Investigations of Potentially Useful Equipment.	76
4.1 Rotor/Stator Colloid Mill	76
4.2 Membrane Filter and Coalescer.	76
4.3 High-Pressure Jet Stream and Vibrating Reed	77
5. Summary of Shear Tests.	79
6. Chemical Demulsification	79
7. Recovered JP-4 Quality.	81
SUMMARY OF RESULTS	83
CONCLUSIONS.	89
RECOMMENDATIONS	90
LITERATURE CITED	91

	<u>Page</u>
APPENDIXES	
I. Emulsifier Neutralization Requirement.	93
II. Yield Stress Value	94
III. Patent Coverage	96
IV. Thermal Conductivity	98
V. Microbial Resistance	104
DISTRIBUTION	110

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Yield Stress Change With Age of MEF-2 Emulsion at 77°F.	45
2	Centrifuged MEF-2	52
3	Migration of Emulsifier -- Activity as a Function of Time at 500 g's	53
4	Wire Resistance Change vs Applied Current	57
5	77°F Evaporation Rate of MEF-1 and MEF-2 JP-4 Fuel Emulsions.	68
6	140°F Evaporation Rate of MEF-1 and MEF-2 JP-4 Fuel Emulsions.	69
7	Yield Value vs Penetration	95
8	Preferred MEF Formulations	97
9	Preferred MEF Formulations	97
10	Preferred MEF Formulations	97
11	Preferred MEF Formulations	97
12	Preferred MEF Formulations	97
13	Sample Container for Test Apparatus	99
14	Schematic of Electrical Measuring Apparatus.	100
15	Thermal Conductivity Apparatus	101
16	Growth Curves of <i>Pseudomonas aeruginosa</i> in the Aqueous Phases of Test and Control Systems.	106

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	MEF Emulsion Matrix	5
II	Matrix Emulsion Stabilities.	6
III	Formulations of Maximum Thermal Stability . .	10
IV	Effect of Rate of Cooling on Emulsion Stability.	12
V	Effect of pH.	13
VI	Effect of Excess Acetic Acid	15
VII	Optimum Emulsions - Droplet Size, Yield Value, and Stability Tests	16
VIII	Stability Consistencies of Emulsions With Identical Formulations, Prepared Same Day . .	19
IX	Coupling Agent Screening.	21
X	Alcohol Coupling Agent Emulsions, Stability .	22
XI	Alcohol Coupling Agent Emulsions, Stability .	23
XII	Effect of pH.	24
XIII	Mild Steel Corrosion Test - Half Immersion. .	27
XIV	Mild Steel and Brass Corrosion Tests - Weight Change Measurement - Metal Coupons Half-Immersed	29
XV	Matrix Emulsions Prepared With New Emulsifiers	31
XVI	Emulsifier Amine Substitution - Effect on Emulsion Stability.	33
XVII	Emulsifier Amine Substitution - Effect on Low-Temperature Emulsion Viscosity	34
XVIII	Amine Content in Technical Gleyl Amines From Various Sources	35
XIX	MEF-2 Candidate Emulsions - Mild Steel and Brass Corrosion Weight Change Measurement - Metal Coupons Half-Immersed.	37

<u>Table</u>	<u>Page</u>
XX Emulsifier Acid Content Effect on Corrosion, pH, and Stability	39
XXI MEF-2 Candidate Emulsions - Droplet Size, Yield Value, and Stability Tests	41
XXII Matrix Formulation Stabilities.	44
XXIII Yield Stress Change With Age	44
XXIV Specific Gravity Change With Age	46
XXV Concentration of C ¹⁴ -Labeled Glycolic Acid in Recovered JP-4	48
XXVI Oleyl Amine Solubility	49
XXVII Droplet Size Variation With Age	50
XXVIII Emulsifier Migration - 500 g's.	51
XXIX Agitation After Aging.	55
XXX Heat Transfer Data.	60
XXXI Surface Free-Energy of MEF-2 Emulsion	63
XXXII Quantitative Corrosion Tests in MEF-2 Emulsion	65
XXXIII Elastomer Compatibility - O-Ring Resistance to JP-4 and MEF-2	67
XXXIV Gum in Shear-Recovered Fuel.	82
XXXV Experimental Data - Thermal Conductivity	103
XXXVI Response of a <i>Hormodendrum</i> sp. in Fluid Cultures Containing Salts Solution Plus JP-4 Fuel or MEF-2 Emulsion	108
XXXVII Growth of <i>Hormodendrum</i> sp. in Solid Media Inoculated by the Pour Plate Method	108

INTRODUCTION

A JP-4 emulsion termed Alamac H26D (hydrogenated tallow amine acetate emulsifier) was developed under a previous contract. This formulation is herein termed MEF (for Monsanto Emulsified Fuel), and improvements made are designated by dash numbers, e.g., MEF-1, etc.

The previous contract resulted in the development of a JP-4 emulsion formulation which satisfactorily reduced the uncontrolled flame and fire properties of JP-4. However, under the press of developing a satisfactory formulation and qualifying it, time did not permit optimization of the product. This emulsion, termed MEF, while satisfactory from the standpoint of flame and fire suppression, required improvement in low-temperature stability, change to minimize the effect of temperature upon yield stress (it became solid at -30°F), and reduction in its corrosive character. These changes represent an essential portion of Phase I of this program.

Phase II of this contract comprises the development of design concepts for the demulsification and recovery of JP-4. The earlier contract demonstrated that the MEF product could quickly and effectively be broken chemically by reaction with ammonium hydroxide. However, under these conditions the tallow amine remained quantitatively in the recovered fuel, and removal of the amine was accomplished by columnar adsorption on activated clay, logistically an undesirable procedure. Exploratory attempts at recovery by mechanically shearing the emulsion were unsatisfactory, even though this approach should have provided an essentially amine-free fuel. Therefore, all methods which used shear in some form were to be investigated to provide a method capable of being scaled up to a rate of JP-4 recovery of 500 gpm.

DEVELOPMENT OF PROBLEM

The prior contract resulted in the development of a thermally stable fuel emulsion, MEF, which in general met the contract formulation requirements. However, that contract did not permit optimization of the formulation, and the current contract contains this as one of its objectives. The ideal formulation must at least meet minimal thermal stability and yield stress requirements but should comprise a maximum content of JP-4, with minimum amounts of external phase components. To assure complete coverage under Phase I of all the component variables, a display matrix was developed; from this, essentially all the formulations were prepared and evaluated, primarily for thermal stability.

The matrix selected was based upon the following concepts. The MEF formulation contains an external non-fuel phase consisting of ethylene glycol and water in which is dissolved the requisite proportion of tallow amine acetate. For analytical and preparative purposes, the systems consist of the ratio of ethylene glycol (EG)/water, external phase (XP)/JP-4, and emulsifier content. These were investigated for rheological and thermal stability characteristics for the following formulation ratios and variations:

EG/water - 50, 62.5, 75, 87.5 and 100 wt %

XP/JP-4 - 97.0, 97.5, 98.0, 98.5 wt %

Emulsifier - 0.15, 0.20, 0.25, 0.3, 0.5 wt %
of total fuel emulsion

Based upon the thermal stability data, 15 formulations, including the original MEF, were prepared and aged 30 days at -30°F, 77°F, and 140°F. Stability was recorded, and yield stress values were taken before and after aging. Additionally, these formulations were examined microscopically to determine emulsion globule size, to ascertain whether this factor had a bearing on stability.

These data were analyzed, and the preferred interim emulsion, MEF-1, was selected.

At this point, improvement in corrosion control and yield stress values was initiated. Indications from previous emulsion preparation were that formulations containing the anti-icing additive (AIA), methyl cellosolve, were more homogeneous and stable than those with the additive absent. Since coupling agents such as the AIA are frequently aids to rate of emulsification and improved stability, a series of these compounds was tested.

Another problem with MEF and MEF-1 was that of corrosion, even when the amount of excess acetic acid used to form the tallow amine acetate was minimized. Other organic acids were therefore substituted, and the corrosivity of these formulations was determined.

A requirement for production purposes is that more than a single source of emulsifier be available; and when several types of tallow amine were examined, one containing a considerable amount of oleyl amine (the more liquid, unsaturated equivalent of tallow amine) was found to give more stable emulsions. Oleyl amine from several sources was evaluated to provide multiple suppliers.

The MEF-1 formulation was then optimized by substituting glycolic acid for acetic acid, thus reducing corrosion to a minimum. Thermal stability testing of the oleyl amine glycolate as for MEF-1 resulted in a preferred composition, MEF-2.

Following development of the MEF-2 formulation, the following properties were determined: yield stress, specific gravity, droplet size change with age, emulsifier solubility and migration, agitation effect after aging, heat transfer coefficient, surface free-energy, corrosion and elastomer compatibility, vapor loss, and microbial resistance.

The objective of Phase II was to develop a method to break the emulsion at a rate of up to 500 gpm to provide JP-4 equivalent to military-specification quality.

EXPERIMENTAL DATA AND DISCUSSION

PHASE I. MEF-1 DEVELOPMENT

1. Emulsion Matrix

In compliance with contract requirements, an all-inclusive formulation matrix based upon the tallow amine acetate formulation was prepared to cover the following parameters:

Ethylene glycol (EG)/water ratio - 50.0, 62.5, 75.0, 87.5 and 100 weight %

Emulsifier content - 0.15, 0.20, 0.25, 0.30, 0.50 weight %

External phase (XP)/JP-4 ratio - 97.0, 97.5, 98.0, 98.5 weight %

The formulation matrix is shown in Table I, which contains the following additional external phase percentages: 3.5, 4.0, and 4.14 which were added when unsatisfactory thermal stability values were obtained for the lower XP ratios. All formulations were prepared in a standard manner, producing about 2-quart (1400-g) quantities.

2. Matrix Emulsion Stabilities

An obvious first requirement was that it be possible to prepare emulsions within the prescribed parameters, and it became apparent that at least 2.5% XP and 0.20% emulsifier would be required to form emulsions. Once emulsions were formed, thermal stability tests were made for 7 days at 140°F, 77°F, and -50°F levels. These data (Table II) showed that none of the 120 emulsions was stable at the lower temperature, and subsequent tests were made at -30°F as a more reasonable level at which differentiation could be attained than the -30°F level.

Most of the emulsions containing 3.0% external phase were easy to make. The exceptions were those containing very low and very high amounts of surfactant, as well as those containing all ethylene glycol. The 0.5% surfactant emulsions went through a severe sluggish, chunky stage during preparation. The 100% ethylene glycol emulsions either would not make or were highly unstable. In general, the emulsions containing the most water were more stable at 140°F while those containing more ethylene glycol were more stable at -30°F, as might have been expected.

TABLE 1. MRP EMULSION MATRIX

TABLE I. MDP EMULSION MATRIX																					
Oil + H ₂ O + Emulsifier	3% External Phase					2.5% External Phase					2% External Phase					1.5% External Phase					
	50%	62.5%	75%	87.5%	100%	50%	62.5%	75%	87.5%	100%	50%	62.5%	75%	87.5%	100%	50%	62.5%	75%	87.5%	100%	
0.15	No.	1	2	3	4	5	26	27	28	29	30	51	52	53	54	55	76	77	78	79	80
	\$ EG	1.43	1.78	2.14	2.49	2.85	1.16	1.47	1.76	2.05	2.35	0.93	1.16	1.39	1.62	1.85	0.68	0.84	1.01	1.18	1.35
	\$ H ₂ O	1.42	1.67	0.71	0.36	0.00	1.17	0.88	0.59	0.29	0.00	0.92	0.69	0.46	0.23	0.00	0.57	0.51	0.34	0.17	0.00
0.20	No.	6	7	8	9	10	31	32	33	34	35	56	57	58	59	60	81	82	83	84	85
	\$ EG	1.40	1.75	2.10	2.45	2.80	1.15	1.44	1.73	2.01	2.30	0.90	1.13	1.35	1.58	1.80	0.65	0.81	0.96	1.14	1.30
	\$ H ₂ O	1.40	1.05	0.70	0.35	0.00	1.15	0.86	0.57	0.29	0.00	0.90	0.67	0.45	0.22	0.00	0.65	0.49	0.32	0.16	0.00
0.25	No.	11	12	13	14	15	36	37	38	39	40	61	62	63	64	65	86	87	88	89	90
	\$ EG	1.38	1.72	2.06	2.41	2.75	1.13	1.41	1.69	1.97	2.25	0.82	1.09	1.31	1.53	1.75	0.63	0.78	0.94	1.09	1.25
	\$ H ₂ O	1.37	1.03	0.69	0.34	0.00	1.12	0.84	0.56	0.26	0.00	0.87	0.66	0.44	0.22	0.00	0.62	0.47	0.31	0.16	0.00
0.30	No.	16	17	18	19	20	41	42	43	44	45	66	67	68	69	70	91	92	93	94	95
	\$ EG	1.35	1.69	2.02	2.36	2.70	1.10	1.38	1.65	1.93	2.20	0.85	1.06	1.27	1.49	1.70	0.60	0.75	0.90	1.05	1.20
	\$ H ₂ O	1.35	1.01	0.68	0.34	0.00	1.10	0.82	0.55	0.27	0.00	0.85	0.64	0.43	0.21	0.00	0.50	0.45	0.30	0.15	0.00
0.50	No.	21	22	23	24	25	46	47	48	49	50	71	72	73	74	75	96	97	98	99	100
	\$ EG	1.25	1.56	1.88	2.19	2.50	1.00	1.25	1.50	1.75	2.00	0.75	0.94	1.13	1.31	1.50	0.50	0.63	0.75	0.88	1.00
	\$ H ₂ O	1.25	0.94	0.62	0.31	0.00	1.00	0.75	0.50	0.25	0.00	0.75	0.56	0.37	0.19	0.00	0.50	0.37	0.25	0.12	0.00
Oil + H ₂ O + Emulsifier	3.5% External Phase					4.0% External Phase					4.5% External Phase					5.0% External Phase					
	25%	37.5%	50%	62.5%	75%	25%	37.5%	50%	62.5%	75%	25%	37.5%	50%	62.5%	75%	25%	37.5%	50%	62.5%	75%	
0.15	No.	101	102	103	104	105	132	133	134	135	136	137	138	139	140	141	163	164	165	166	167
	\$ EG	1.68	2.09	2.51	2.93	3.35	1.93	2.41	2.89	3.37	3.85	1.90	2.38	2.85	3.33	3.80	1.44	1.92	2.40	2.88	3.36
	\$ H ₂ O	1.67	1.26	0.84	0.42	0.00	1.92	1.44	0.96	0.48	0.00	1.90	1.42	0.95	0.47	0.00	1.40	1.87	2.34	2.81	3.28
0.20	No.	106	107	108	109	110	137	138	139	140	141	137	138	139	140	141	163	164	165	166	167
	\$ EG	1.65	2.06	2.47	2.88	3.30	1.90	2.38	2.85	3.33	3.80	1.90	2.38	2.85	3.33	3.80	1.44	1.92	2.40	2.88	3.36
	\$ H ₂ O	1.65	1.24	0.83	0.42	0.00	1.90	1.42	0.95	0.47	0.00	1.90	1.42	0.95	0.47	0.00	1.40	1.87	2.34	2.81	3.28
0.25	No.	111	112	113	114	115	116	117	118	119	120	142	143	144	145	146	163	164	165	166	167
	\$ EG	0.82	1.22	1.62	2.03	2.43	2.84	3.25	0.94	1.41	1.88	0.94	1.41	1.88	2.34	2.81	1.44	1.92	2.40	2.88	3.36
	\$ H ₂ O	2.43	2.03	1.63	1.22	0.82	0.41	0.00	2.81	2.34	1.87	2.81	2.34	1.87	1.41	0.94	0.46	0.92	1.39	1.86	2.33
0.30	No.	118	119	120	121	122	123	124	149	150	151	149	150	151	152	153	163	164	165	166	167
	\$ EG	0.80	1.20	1.60	2.00	2.40	2.80	3.20	0.93	1.39	1.85	0.93	1.39	1.85	2.31	2.77	1.44	1.92	2.40	2.88	3.36
	\$ H ₂ O	2.40	2.00	1.60	1.20	0.80	0.40	0.00	2.77	2.31	1.85	2.77	2.31	1.85	1.39	0.93	0.46	0.92	1.39	1.86	2.33
0.40	No.	119-1	120	121	122	123	124	125	150-1	151-1	152-1	150-1	151-1	152-1	153-1	154-1	165	166	167	168	169
	\$ EG	1.35	1.75	2.15	2.55	2.95	3.35	3.75	1.35	1.75	2.15	1.35	1.75	2.15	2.55	2.95	1.40	1.80	2.20	2.60	3.00
	\$ H ₂ O	2.25	1.85	1.45	1.05	0.65	0.25	0.00	2.25	1.85	1.45	2.25	1.85	1.45	1.05	0.65	2.34	1.87	2.34	2.81	3.28
0.50	No.	125	126	127	128	129	130	131	156	157	158	156	157	158	159	160	167	168	169	170	171
	\$ EG	0.75	1.13	1.50	1.87	2.25	2.62	3.00	0.87	1.24	1.61	0.87	1.24	1.61	1.98	2.35	1.44	1.82	2.19	2.56	2.93
	\$ H ₂ O	2.25	1.87	1.50	1.13	0.75	0.38	0.00	2.63	2.19	1.75	2.63	2.19	1.75	1.31	0.87	0.44	0.92	1.39	1.86	2.33
Ethylene glycol																					

TABLE 12. MATRIX EMULSION STABILITIES

Emulsion Phase	3.5%					2.5%					2.0%					1.5%				
	50%	62.5%	75%	87.5%	100%	50%	62.5%	75%	87.5%	100%	50%	62.5%	75%	87.5%	100%	50%	62.5%	75%	87.5%	100%
0.15	No. 1 Yes 1 No 1 Yes 1 No 1 Yes 1 No 1	2 Yes 3 Yes 4 Yes 5 Yes 6 Yes 7 Yes	3 Yes 4 Yes 5 Yes 6 Yes 7 Yes 8 Yes	4 No 5 No 6 No 7 No 8 No 9 No	5 No 6 No 7 No 8 No 9 No 10 No	26 Yes 27 Yes 28 No 29 No 30 No 31 No	27 Yes 28 No 29 No 30 No 31 No 32 No	28 No 29 No 30 No 31 No 32 No 33 No	29 No 30 No 31 No 32 No 33 No 34 No	30 No 31 No 32 No 33 No 34 No 35 No	51 Yes 52 No 53 No 54 No 55 No 56 No	52 No 53 No 54 No 55 No 56 No 57 No	53 No 54 No 55 No 56 No 57 No 58 No	54 No 55 No 56 No 57 No 58 No 59 No	55 No 56 No 57 No 58 No 59 No 60 No	76 No 77 No 78 No 79 No 80 No 81 No	77 No 78 No 79 No 80 No 81 No 82 No	78 No 79 No 80 No 81 No 82 No 83 No	79 No 80 No 81 No 82 No 83 No 84 No	80 No 81 No 82 No 83 No 84 No 85 No
0.20	No. 6 Yes 6 No 6 Yes 6 No 6 Yes 6 No 6	7 Yes 8 Yes 9 Yes 10 Yes 11 Yes 12 Yes	8 Yes 9 Yes 10 Yes 11 Yes 12 Yes 13 Yes	9 No 10 No 11 No 12 No 13 No 14 No	10 No 11 No 12 No 13 No 14 No 15 No	31 Yes 32 Yes 33 Yes 34 Yes 35 Yes 36 Yes	32 Yes 33 No 34 No 35 No 36 No 37 No	33 No 34 No 35 No 36 No 37 No 38 No	34 No 35 No 36 No 37 No 38 No 39 No	35 No 36 No 37 No 38 No 39 No 40 No	46 Yes 47 No 48 No 49 No 50 No 51 No	47 No 48 No 49 No 50 No 51 No 52 No	48 No 49 No 50 No 51 No 52 No 53 No	49 No 50 No 51 No 52 No 53 No 54 No	50 No 51 No 52 No 53 No 54 No 55 No	86 No 87 No 88 No 89 No 90 No 91 No	87 No 88 No 89 No 90 No 91 No 92 No	88 No 89 No 90 No 91 No 92 No 93 No	89 No 90 No 91 No 92 No 93 No 94 No	90 No 91 No 92 No 93 No 94 No 95 No
0.30	No. 11 Yes 11 No 11 Yes 11 No 11 Yes 11 No 11	12 Yes 13 Yes 14 Yes 15 Yes 16 Yes 17 Yes	13 Yes 14 Yes 15 Yes 16 Yes 17 Yes 18 Yes	14 No 15 No 16 No 17 No 18 No 19 No	15 No 16 No 17 No 18 No 19 No 20 No	36 Yes 37 Yes 38 Yes 39 Yes 40 Yes 41 Yes	37 Yes 38 No 39 No 40 No 41 No 42 No	38 No 39 No 40 No 41 No 42 No 43 No	39 No 40 No 41 No 42 No 43 No 44 No	40 No 41 No 42 No 43 No 44 No 45 No	61 Yes 62 No 63 No 64 No 65 No 66 No	62 No 63 No 64 No 65 No 66 No 67 No	63 No 64 No 65 No 66 No 67 No 68 No	64 No 65 No 66 No 67 No 68 No 69 No	65 No 66 No 67 No 68 No 69 No 70 No	96 No 97 No 98 No 99 No 100 No 101 No	97 No 98 No 99 No 100 No 101 No 102 No	98 No 99 No 100 No 101 No 102 No 103 No	99 No 100 No 101 No 102 No 103 No 104 No	100 No 101 No 102 No 103 No 104 No 105 No

Table II - Continued

External Phase -		4.0% (Some Repeats)										3.5%		3.0%		2.5%		2.0%	
Emulsion No.		163	164	MEF	165	166	167	168	150	150-1	151	151-1	157	158	158-1	159-1	119-1	126	
% Emulsifier		0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.3	0.4	0.3	0.4	0.5	0.5	0.6	0.6	0.4	0.5	-
% EO/H ₂ O Ratio		37.5	50	54	37.5	50	37.5	50	37.5	37.5	50	50	37.5	50	37.5	37.5	37.5	37.5	0.4
% EO		1.44	1.92	2.02	1.40	1.87	1.37	1.82	1.39	1.35	1.85	1.80	1.31	1.75	1.70	1.28	1.16	1.13	0.98
% H ₂ O		2.80	1.92	1.72	2.34	1.87	2.27	1.82	2.31	2.25	1.85	1.80	2.19	1.75	1.70	2.12	1.94	1.87	1.62
% Excess Acetic Acid		4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	2.2	4.4	2.2
Stability - 7 Days		syn	1	1	syn	7	8	8	7	1	1	1	8	7	8	8	7	8	7
140°F		S	S	1	S	1	S	7	1	1	1	1	S	7	8	7	7	8	7
-30°F																			

see - Ability to prepare.

f 1 - unstable within 1 day

h 7 - unstable between 1 and 7 days

e 8 - stable at least 7 days

d syn - Syneresis

c Stable at -30°F

f Slow

g Normal

As the external phase was lowered from 3.0%, the emulsions took longer to make, until at 1.5% very few emulsions could be made. Those that were made proved to be highly unstable.

The only emulsion that was stable at -30°F for 7 days was No. 60. But this emulsion was so unstable at higher temperatures that it had to be shaken back into emulsion form at 77°F before it could be placed in the -30°F cabinet. The stabilities of the matrix emulsions are shown in Table II (blank spaces are emulsions not made because of failure certainty).

The matrix experimentation was expanded to include emulsions containing 3.5%, 4.0%, and 4.14% external phase (Table I). The emulsifier content was again varied from 0.15% to 0.50%, while the remaining external phase ranged from 25% to 100% EG (any remainder water). Emulsions containing less than 50% EG were not prepared with less than 0.25% emulsifier, since other emulsions of this content had demonstrated little stability.

The stability results through 4.0% XP show that none of the emulsions are completely stable at both -30°F and 140°F (Table II). Several emulsions are stable at -30°F, but none of these lasted 7 days at 140°F without separating a small amount of JP-4. Emulsions Nos. 126 and 157 can be considered to be almost stable at both temperatures, but 7 days of 140°F exposure slowly produced a film of JP-4 on both emulsions which settled into a pool of several drops as the emulsions cooled down to 77°F. This condition may be caused by syneresis (contraction of the emulsion), and it is indicated in the tables by the abbreviation "syn". Adsorption of a small amount of emulsifier to the container walls may also have contributed to this JP-4 exudation.

The 4.14% external phase of the MEF emulsion was not included in the original matrix experimentation. However, it is hard to believe that 0.14% is the difference between a stable and an unstable emulsion. Emulsions Nos. 151 and 158 are the closest to the MEF formulation of 0.39% emulsifier and 54% EG, but neither of these emulsions was stable at the temperature extremes.

In general, examination of the 4% XP and 0.3% to 0.5% emulsifier data shows that the 0.4% and 0.5% emulsifier formulations are superior, and that either the 0.5% or 0.4% emulsifier level, with 37.5% EG content of the XP, provides the greatest thermal stability. The formulations of Table III were the most stable of those tested.

TABLE III. FORMULATIONS OF MAXIMUM THERMAL STABILITY							
	126	157	163	Formula		167	MEF
				165	157-A ^a		
% External Phase	3.5	4.0	4.14	4.14	4.0	4.14	4.14
% Emulsifier	0.5	0.5	0.3	0.4	0.5	0.5	0.4
% EG	37.5	37.5	37.5	37.5	37.5	37.5	54.0
% Excess Acetic Acid	4.4	4.4	4.4	4.4	2.2	4.4	2.2
7-Day Stability							
77°F	S ^b	S	S	S	S	S	S
140°F	syn ^c	syn	syn	syn	S	S	syn
-30°F	S	S	S	S	S	S	S
<p>^a A refers to change in excess acetic acid; see formulation.</p> <p>^b S - Stable at least 7 days.</p> <p>^c Syneresis.</p> <p>Corrosion caused by MEF may be a function of the amount of excess acetic acid used to neutralize and solubilize the amine. Consequently, the effect upon stability by reducing the excess acidity was determined.</p>							

3. Low-Temperature Storage Investigation

Initial investigation of the 100-matrix formulations failed to show that any of them passed the -50°F level. Since work on the previous contract had shown that MEF was reasonably stable at -20°F , an intermediate -40°F level was selected for test; here too the compositions separated. At -30°F some of the emulsions proved stable; this temperature was then used in subsequent screening.

In one instance formulations were stored about a day at -16°F before being subjected to the -30°F condition. The emulsions proved stable when subsequently removed to the -30°F condition. To determine whether this had significant effect, the formulations shown in Table IV were subjected to a precooling cycle at -16°F for the number of days indicated before being transferred to the -30°F condition.

The data show conclusively that it is the thermal shock more than the low temperature which causes the apparent lack of stability. It is believed that the emulsions have relatively low thermal transmission characteristics, so that cold temperature storage would result in slow heat transfer, or preconditioning. Expressed differently, under usual storage conditions it is unlikely that a shock from 77°F to -30°F would affect large volumes of emulsion. It is also unlikely that large container size and low heat transfer rate would have the same effect as precooling.

4. Effect of pH and Acidity Excess

Since MEF is acidic and tends to cause mild steel corrosion, attempts were made to make the emulsions more neutral and possibly less corrosive. The approach selected was to determine the effect of the tallow amine salt constitution as a function of excess acetic acid content on the character of the emulsion.

Salts of relatively strong acids and weak bases hydrolyze in aqueous solution to form acidic media. While acetic acid is not strong as compared with inorganic acids such as hydrochloric, for example, it nevertheless is a comparatively strong organic acid. Amines are relatively weak bases as compared with ammonia, and though they form salts with acids, upon hydrolysis the long chain amines may become water insoluble; hence, amines offer no real basic reaction in aqueous media. For these reasons, tallow amine acetate will hydrolyze to form acidic (hence potentially corrosive) solutions. Table V shows the effect upon pH and the thermal stability of emulsions prepared from compositions where excess amine was used to attempt to raise the pH to neutrality. When stoichiometric

TABLE IV. EFFECT OF RATE OF COOLING ON EMULSION STABILITY												
	Days	Emulsion No.										
		158	157	150	150-1	119-1	17-1	42-1				
% XP		4.0	4.0	4.0	4.0	4.0	3.5	3.0	2.5			
% Emulsifier		0.5	0.5	0.3	0.4	0.4	0.4	0.4	0.4			
% EG		50.0	37.5	37.5	37.5	37.5	37.5	37.5	37.5			
Exposure	1	10%	5%	20%	2%	5%	10%	2%	15%	30%		
-30°F only	7	20%	15%	20%	2%	15%	20%	5%	25%	50%		
Precooling at												
-16°F for		4	4	1	1	3	3	3	3	3		
days shown												
Exposure -30°F	1	+	+	+	+	+	syn	+	+	10%		
after -16°F	7	+	+	syn	syn	+	50%	5%	+	40%		
precooling												

TABLE V. EFFECT OF pH										
Emulsion No.	Excess Amine	pH of XP of 3% of JP-4		pH of XP of 9% of JP-4	Emulsion pH 100% JP-4	Emulsion Stability - 1 & 7 Days				
						77°F	140°F	-30°F		
						(1)	(7)	(1)	(7)	(7)
16	0.0	5.80	--	--	5.80	^a +	+	5%	20%	^b
16-1	4.8	6.60	6.60	6.60	6.35	+	+	2%	25%	
16-2	10.0	6.95	6.60	6.60	6.40	+	+	5%	50%	
16-3	20.6	7.20	7.20	7.20	6.35	+	+	5%	50%	
16-4	-5.8					+	+	5%	20%	
22	0.0					+	+	+	sepn	
22-1	-5.8					+	+	1%	10%	
<hr/>										
^a + - stable						No.16	No.22	No.22-1		
^b % - JP-4 separation percent										
					% XP	3	3	3	3	
					% EG	50	62.5	37.5		
					% Emulsifier	0.3	0.5	0.5		

amounts of acetic acid and tallow amine were used, the emulsion pH was slightly acid at 5.80. Excess amine, and in two cases excess acid, was used. Excess amine increased the pH but simultaneously reduced thermal stability, whereas stoichiometric or slightly acidic emulsifier usage tended to produce more stable emulsions.

Further, to define the extent of acetic acid excess, five formulations were tested at 4.4, 2.2, and 0 excess of acetic acid in the preparation of the emulsifier. Table VI shows that generally a 2.2% excess of acetic acid, though it leaves the emulsion acid, tends to provide the most thermally stable emulsions. The table shows no 77°F values, since these were stable and failed to differentiate between formulations.

It might be proposed that an optimum value of excess acetic acid nearer stoichiometric, such as 1.1% or 0.5% excess, might more nearly provide a less corrosive medium. The significance of these values and their possible attainment in production is as follows. MEF contains 4.4% excess acetic acid, at which point the amine-acetate salt then contains 18.9% glacial acetic acid. A stoichiometric salt contains 18.1% acid. Since the external phase concentrate consists of the amine salt in ethylene glycol made by adding molten amine to the acetic acid-EG mixture, various EG:emulsifier ratios can be used. One used in this work comprised 2 parts EG to 1 part emulsifier on a 280:140 weight basis. Of the 140 parts, 26.46 parts for the 4.4% excess is the acid, so that the acid represents 6.30% of the total concentrate. On the same basis, but for stoichiometric amounts, the acid amounts to 6.03%. On 100-pound batches there would be a difference in acid weight of 6.30 vs 6.03, possibly within the sensitivity of the scales used for manufacture. Looked at differently, variation in a 100-pound lot of about 1/4 pound would make the difference between 4.4% and 0% excess acid. As a consequence, it was decided that 2.2% and 4.4% excesses of acetic acid would be used for evaluation of the 15 preferred formulations.

5. Formulas for Storage Tests

Based upon the matrix formulation stability and the excess acetic acid data, a number of formulations were selected for the extended storage and stability tests. These formulations were chosen to cover the near-optimal or optimal external phase, emulsifier, ethylene glycol ratio, and excess acetic acid contents with tallow amine as the emulsifier. In certain instances, values on either side of the optimum were included to cover possible variations. The chosen formulations are given in Table VII.

TABLE VII. OPTIMUM EMULSIONS - DROPLET SIZE, YIELD VALUE, AND STABILITY TESTS

Emulsion No.	MEP	157	158	150-1			151-1			150	151	126	167	165	163		157	126
External Phase	4.14	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	3.50	4.14	4.14	4.14	4.14	4.0	3.50
Emulsifier	0.4	0.5	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.5	0.5	0.4	0.3	0.3	0.5	0.5
EG/H ₂ O Ratio (% EG)	54%	37.5	50.0	37.5	37.5	37.5	37.5	50.0	50.0	37.5	50.0	37.5	37.5	37.5	37.5	37.5	37.5	37.5
% Excess Acid	4.4	2.2	2.2	4.4	2.2	2.2	0.0	2.2	2.2	2.2	2.2	2.2	4.4	4.4	4.4	4.4	4.4	4.4
Droplet Size (μ)																		
Range	2-6	1-7	2-5	2-9	1-8	3-7	2-8	2-5	1-7	2-7	1-8	1-5	1-5	1-5	2-10	2-10	1-5	1-5
Median Size	4	4	4	5	5	5	5	4	4	5	4	4	4	4	5	5	4	4
Yield Value Dynes/cm ²																		
Temp. Storage	1460	1460	1650	1700	1260	1460	2900	1270	1140	1600	1380	1370	1310	1310	1250	1390	1810	
Temp. Immediately	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	
0°F 1 day	0°F	0°F	0°F	0°F	0°F	0°F	0°F	0°F	0°F	0°F	0°F	0°F	0°F	0°F	0°F	0°F	0°F	
0°F 30 days	7200	9000	5000	7100	7400	7600	6800	7800	5300	6800	7800	8000	8200	8200	5900	8200	8500	
16°F 30 days	5560	6400	6300	6400	5500	5500	4500	6200	5100	5160	5800	7200	7400	7400	5300	8300	8100	
77°F 30 days	700	900	750	760	750	730	650	700	680	680	730	730	730	620	570	680	880	
140°F 30 days	360	420	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	
Stability																		
Days	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Temp.	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F	77°F
12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12
140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F
140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F	140°F
30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12
30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30

^aFew drops of liquid due to syneresis.

^bNo breakdown.

^cPercent free JP-4.

^dLiquid mixed with all emulsions in this group; MEP & 157 are the two extremes for viscosity.

^eTemperature dropped to about -40°F, causing 50% breakdown in all the emulsions.

Ten representative emulsions were prepared in 1-gallon quantities for the above tests. Two weeks later, 5 additional emulsions were prepared to complete the investigational picture. The Hobart Model C-100 mixer of 2-gallon capacity was used for these preparations.

5.1 Droplet Size

The droplet size range and median value were determined via the microscope for all 15 emulsions on the day of preparation. The thermal stability results of Table VII show no distinct difference between emulsions, even though 151-1 began to break almost immediately after preparation. It appears that droplet size is largely a function of mixing technique rather than stability (Table VII), and its determination will not serve as a satisfactory quality-control method.

5.2 Yield Stress Values

The yield value was determined for all 15 emulsions within an hour of preparation using the revised specification for the purpose (Appendix II). A full 1-quart jar of each emulsion was then stored for 30 days at 140°F, and two leveled 800-milliliter beakers of each emulsion were covered tightly with aluminum foil and stored 30 days at -16°F and -30°F. Prior to the -16°F storage, the beakers of emulsion had been stored overnight at 0°F so that the yield value could be measured at this temperature the following day. The remaining portion of emulsion from the 1-gallon quantity was stored 30 days at 77°F.

At the end of these storage periods, the yield values were again measured at the prescribed temperatures of 77°F for the emulsions stored at 140°F and 77°F, and of 0°F for the emulsions stored at -16°F. The emulsions at -30°F had all broken about 50%, and the yield value could not be determined. The emulsions at 140°F all contained some free JP-4, and the yield values of these could not accurately be determined; the yield values of the thickest and thinnest appearing emulsions were so numerically close that the rest of the emulsions in this group were arbitrarily assigned a yield value of 400 dynes/cm² (see Table VII).

Again there was no significant difference in yield values between emulsions at either high or low temperatures. The one exception was emulsion 151-1, which was very viscous upon preparation and began to break almost immediately. A repeat of this emulsion preparation produced an emulsion of standard viscosity which appeared to be more stable than the first. However, after several hours, it too began to break.

All the emulsions became significantly less viscous after storage at 140°F and 77°F. They were all very viscous at 0°F, both before and after storage, and would not pour or flow.

An experiment was conducted to check on the reproducibility of emulsion stability results. Five emulsions each of the two most preferred formulations were prepared the same day within identical parameters. The standard 7-day stability tests were run at 140°F and -30°F. When a malfunction occurred in the -30°F cabinet and ruined the test, another was started with the remaining emulsion, now 7 days old. These results are shown in Table VIII. It is interesting to note that some of the emulsions, showing either stability or instability in the first abbreviated -30°F test, reversed positions in the second test. Overall, emulsion 157 showed more stability than 150-1.

6. MEP-1 Selection

Expansion of the original matrix of 100 compositions to a total of 168 was necessary to define the parameters controlling thermal stability and included extensions of the external phase and certain formulations at 0.4% emulsifier levels.

Attempts at storage at -50°F were unsuccessful, and a -30°F level was used to provide a degree of differentiation between formulations; even then the formulations proved unsatisfactory.

It was found that preconditioning of emulsion for up to 24 hours at -15°F before plunging into -30°F conditions resulted in much more stable emulsions. As a consequence, it is concluded that thermal shock is a controlling factor in low-temperature stability.

Ease of preparation and thermal stability showed that the external phase was at an optimum at 4.0 weight %. Ratio of ethylene glycol to water was at an optimum at 37.5% glycol to 62.5% water.

At the foregoing levels of external phase and ethylene glycol, an optimum level of 0.5 weight % emulsifier proved to be most satisfactory.

The effect of pH of the external phase and the ratio of acetic acid to tallow amine was investigated, showing that optimum stability was attained at 2.2% excess acid.

Fifteen formulations were selected for extended evaluation, which included thermal stability, yield stress values, and droplet size. Droplet size appeared to be more a function of preparation than of stability and did not appear to lend

TABLE VIII. STABILITY CONSISTENCIES OF EMULSIONS WITH IDENTICAL FORMULATIONS, PREPARED SAME DAY												
Emulsion Number	157					150-1						
% External Phase	4.0					5.0						
% EG/H ₂ O	37.5					37.5						
% Emulsifier	0.5					0.4						
% Excess Acetic Acid	2.2					2.2						
Stability Temp												
Days	140°F		-30°F		-30°F (1 week later) ^a		140°F		-30°F		-30°F (1 week later) ^b	
	1	7	1	7	1	7	1	7	1	7	1	7
Emulsions Prepared												
1	+	+	2%	<u>b</u>	Syn	+	4%	+	+	2%	5%	
2	+	+	+	-	5%	5%	1%	+	3%	5%	10%	
3	+	Syn	+	-	+	+	Syn	+	1%	+	Syn	
4	+	+	2%	-	1%	2%	+	+	1%	3%	5%	
5	+	Syn	1%	-	+	+	Syn	+	2%	+	2%	
^a Emulsion sat at room temperature 1 week before -30°F test.												
^b Cabinet malfunctioned; all emulsions broke about 50% at -40°F.												

itself to quality control. None of the emulsions was stable at -30°F , but all were satisfactory at -16°F . All of the emulsions showed decrease in yield value after a 30-day storage period.

The preferred formulation was comprised of 4.0 weight % external phase, 0.5% emulsifier at 2.2% excess acetic acid, 37.5 weight % ethylene glycol, and 62.5% water. This formulation was superior to the original MEF formulation, and had an initial yield stress of 1460 dynes/cm², which became 6400 after 30 days at -16°F , and 900 after 30 days at 77°F . The emulsion released 15% JP-4 after 12 days at -30°F .

The formulation recommended as MEF-1, resulting from the experimental data cited, has the following composition:

External phase - 4.0 weight %

Ethylene glycol/water weight ratio - 37.5/62.5

Emulsifier - 0.5 weight % at 2.2% acetic acid excess

Improvements in corrosion prevention and thermal stability were based upon this formulation.

MEF-2 DEVELOPMENT

Having optimized the formulation to produce MEF-1, the improvement over the originally recommended formula, other approaches were followed to lead to a final formulation as free as possible from faults such as lack of low-temperature stability and high yield stress, and corrosion. The following sections record these improvements.

7. Coupling Agents

Previous observations had indicated that the anti-icing additive (AIA) in JP-4 fuel, comprising methyl cellosolve, had resulted in an improved MEF, but it was not possible to pursue this lead further at that time. It was suspected that substitution of AIA or another coupling agent (i.e., a fluid which will make two immiscible phases more compatible) for ethylene glycol would improve thermal stability. Consequently, a number of the more likely chemicals of this general nature were chosen and applied to a selected tallow amine acetate formulation. Several were tested and are shown in Tables IX through XII.

Initial tests were made with selected coupling agents used in a formulation approaching the MEF base; e.g., matrix formula 16 comprising 3% external phase, 0.3% tallow amine acetate,

TABLE IX. COUPLING AGENT SCREENING						
Replacing 50% of EG in No. 16 Matrix Emulsion						
Coupling Agent	Emulsion Stability - 3 & 7 Days					
	77°F	140°F	-30°F			
	(3)	(7)	(3)	(7)	(3)	(7)
Methyl cellosolve	+	+	10%	-	40%	-
Carbitol	+	+	15%	-	20%	-
Methyl carbitol	+	+	10%	-	50%	-
Ethylene glycol dimethyl ether	+	+	20%	-	40%	-
Hexylene glycol	75%	-	100%	-	10%	-
Sucrose	+	+	90%	-	+	+
t-Butanol	+	+	5%	-	+	+
Methanol	+	+	5%	-	+	+
Lextrose	+	+	50%	-	20%	-
Dihydroxy acetone	25%	-	100%	-	80%	-
None	+	+	+	5%	20%	-
(+) - stable	% External Phase - 3.0					
(%) - amount breakdown	% Emulsifier - 0.3					
(-) - not determined	Ratio EG/Water - 50/50					

TABLE X. ALCOHOL COUPLING AGENT EMULSIONS, STABILITY											
Matrix No.	External Phase	EG/Water Ratio	% of EG	Coupling Agent	% Emulsifier	Emulsion Stability* - 1 & 7 Days					
						77°F		140°F		-30°F	
						(1)	(7)	(1)	(7)	(1)	(7)
16	3.0	50	20	t-butanol	0.30	+	+	+	10%	+	2%
	3.0	50	20	methanol	0.30	+	+	+	5%	+	+
	3.0	50	50	t-butanol	0.30	+	+	5%	-	+	+
	3.0	50	50	methanol	0.30	+	+	5%	-	+	+
	3.0	50	100	t-butanol	0.30	X	X	X	X	X	X
21	3.0	50	100	methanol	0.30	+	+	40%	-	50%	-
	3.0	50	20	t-butanol	0.50	+	+	+	5%	+	30%
	3.0	50	20	methanol	0.50	+	+	+	1%	?	-
	3.0	50	50	t-butanol	0.50	+	+	+	5%	20%	60%
22	3.0	62.5	20	t-butanol	0.50	+	+	+	2%	20%	-
	3.0	62.5	20	methanol	0.50	X	X	X	X	X	X
	3.0	62.5	47	t-butanol	0.50	+	+	+	5%	20%	-
	3.0	62.5	100	methanol	0.50	20%	-	60%	-	10%	-
* (+) - stable (-) - not determined (%) - breakdown (X) - could not be made											

TABLE XI. ALCOHOL COUPLING AGENT EMULSIONS, STABILITY																
Emulsion No.	151				150				158				157			
	Total External Phase	4.0	+	+	4.0	+	+	+	4.0	+	+	+	4.0	+	+	
% Emulsifier	0.3	0.3	+	+	0.3	+	+	+	0.5	+	+	+	0.5	+	+	
Original % EG/H ₂ O Ratio	50	50	+	+	37.5	+	+	+	50	+	+	+	37.5	+	+	
% EG Replaced by Alcohol	None	None	20	20	None	20	20	20	None	20	20	20	None	20	20	
Alcohol Tested	None	MeOH	Isopropanol	t-BuOH	None	MeOH	Isopropanol	t-BuOH	None	MeOH	Isopropanol	t-BuOH	None	MeOH	Isopropanol t-BuOH	
Stability: 140°F -30°F	2% 40%	20% 30%	3% 15%	5% 5%	+	2% 50%	1% +	1% 1%	2% 5%	2% 10%	1% 5%	1% +	+	+	+	
Total External Phase	4.0	4.0	+	+	4.0	+	+	+	4.0	+	+	+	4.0	+	+	
% Emulsifier	0.3	0.3	+	+	0.3	+	+	+	0.5	+	+	+	0.5	+	+	
Original % EG/H ₂ O Ratio	50	50	+	+	37.5	+	+	+	50	+	+	+	37.5	+	+	
% EG Replaced by Alcohol	None	50	50	50	None	50	50	50	None	50	50	50	None	50	50	
Alcohol Tested	None	MeOH	Isopropanol	t-BuOH	None	MeOH	Isopropanol	t-BuOH	None	MeOH	Isopropanol	t-BuOH	None	MeOH	Isopropanol t-BuOH	
Stability: 140°F -30°F	2% 40%	5% +	2% 5%	5% +	+	1% 25%	+	Syn	2% 5%	5% 20%	+	1% +	+	2% 50%	1% 1%	
MeOH - methanol t-BuOH - t-butanol																

TABLE XII. EFFECT OF pH Emulsion No. i6 Base									
% Emulsifier	% HAC ^a Emulsifier	% Excess Amine	pH of		Emulsion pH 100% JP-4	Emulsion Stability, 1 & 7 Days			
			XP @ 3% of JP-4	XP @ 9% of JP-4		77°F (1)	140°F (1)	170°F (1)	-30°F (1)
0.3	18.9	0.0	5.80	-	5.80	+	+	+	20%
0.3	18.0	4.8	6.60	6.60	6.35	+	+	2%	25%
0.3	17.0	10.0	6.95	6.60	6.40	+	+	5%	50%
0.3	15.0	20.6	7.20	7.20	6.35	+	+	5%	50%
0.3	20.0	-5.8				+	+	5%	20%
0.5	20.0	-5.8				+	+	+	1% 10%
^a Acetic acid ^b + - stable % - breakdown percent									

and 50/50 ratio of EG/water. These data (Table IX) show that t-butanol improved the overall emulsion stability. While not affected at 140°F, the emulsion was stable for 7 days at -30°F.

Methanol was subsequently tried and was found to work equally as well as, or better than, t-butanol; also, emulsion formation seemed slightly improved as compared with t-butanol. Both alcohols caused bypassing of the early "chunky" stage which occurs in preparing MEF emulsion. Both alcohols were tested at various concentrations in three "type" formulations (Nos. 16, 21, and 22); the stability results are shown in Table X.

An attempt was made to prepare the amine acetate emulsifier in water rather than in EG, which is standard procedure. This would allow the use of a more emulsifier-dilute XPC, since water is the major external phase constituent in MEF-1. However, the emulsifier precipitated in the water when the amine and acid were reacted and would not dissolve even with mild heating. This result seemed to rule out the possibility of a 100% water emulsion and illustrated the value of EG as a coupling agent between the emulsifier and water.

Table XI shows the effect of varying amounts of methanol, isopropanol, and t-butanol on the stability of other matrix formulations. The isopropyl and tertiary butyl alcohols generally produced emulsions with about the same stability as the parent emulsions, while methanol generally gave less stable emulsions. Failure to significantly improve stability does not warrant the use of an alcohol in emulsions.

8. Corrosion

8.1 Emulsion pH - Effect of Excess Tallow Amine

Emulsion MEF was found to have a pH range of 5.5-6.0. This acidity is probably the cause of mild steel corrosion. Various external phase concentrates were therefore prepared with excess tallow amine to obtain an emulsion with a pH higher than 7.0. Matrix emulsion No. 16 was prepared in each case, and the pH was measured after varying amounts of JP-4 were added (Table XII).

While excess amine raised the pH of the external phase, cumulative additions of JP-4 gradually solubilized the excess amine until an acid condition was again produced in the final emulsion.

Reduced stability of the emulsions resulted as excess hydrogenated tallow amine was added.

These data indicate that, because of emulsion instability, corrosion cannot be controlled by excess amine additions to the tallow amine acetate emulsions; therefore, other approaches were sought.

8.2 Additives

A short literature search showed that there were no reported additives that would completely prevent mild steel corrosion in an acetic acid environment. Many compounds were suggested that might retard corrosion by a protective adsorption on the metal, and these were tried in an emulsion system. An amount of various potential inhibitors equal to 0.5% of the external phase, or 200 ppm of the total emulsion, was added during emulsion preparation. Cleaned 1- x 3 inch mild steel coupons were half-immersed in these emulsions, which were then stored either 1 day at 140°F or 1 week at 77°F. Metal coupons were also immersed in emulsions containing either alcohol coupling agents, various amounts of external phase constituents, or emulsifier containing an acetic acid substitute. The severity of corrosion at the end of the test periods was visually estimated, and a numerical rating was given each emulsion (0 for no corrosion). The results are shown in Table XIII.

Most of the corrosion at 77°F occurred at the emulsion-air interface or below, while the corrosion at 140°F occurred at the emulsion-air interface or above. None of the additives significantly slowed corrosion at 140°F, and only cyclohexylamine reduced corrosion at 77°F. However, this additive greatly reduced both the emulsion stability and viscosity. Emulsions containing the most water and emulsifier caused the fastest and most severe corrosion at 77°F, while no difference was noted at 140°F. Alcohol coupling agents had little or no effect on the corrosiveness of the emulsion.

Since none of the more usual additives appeared to control corrosion, the next step was to change the acid used to neutralize the amine, with the hope that the acid hydrolysis product would be less corrosive than acetic acid.

8.3 Replacement of Acetic Acid in the Amine Acetate

Previously reported data showed that stoichiometric neutralization of tallow amine resulted in lowered thermal stability but possibly improved corrosion characteristics. Near-optimum thermal stability was achieved using a 2.2% excess amount of acetic acid for neutralization, though retaining the undesirable corrosion factor. To correct this feature, it was conceived that a change in the terminal grouping of a short chain

Emulsion + Additive ^a	Temperature									
	140°F					77°F				
	Rating ^b 1 Day	3 Days	7 Days	Rust Description	Rating ^b 1 Day	3 Days	7 Days	Rust Description	Rating ^b 1 Day	3 Days
JP-4 Fuel	0	-	0	None visible to eye	0	-	-	None	0	-
MEP (4.4% excess HAC)	15	-	-	Mostly at interface, spotty elsewhere	0	-	1	Rust on edges only	0	-
MEP (2.2% excess HAC)	15	-	-	Mostly at interface, spotty elsewhere	0	-	0 ^d	Barely a trace on edge	0	-
MEP (0.0% excess HAC)	15	-	-	Mostly at interface, spotty elsewhere	0	-	1	Few spots on edges	0	-
147A ^c (2.2% excess)	18	-	-	Mostly at interface & above	10	-	15	Heavy rust below surface	10	-
147A (6.0% deficiency)	-	15	-	Mostly at interface & above	-	-	-	Rust from edges spread	-	-
142A (2.2% excess)	15	-	-	Mostly at interface	5	-	5	Heavy edge rust	5	-
142A (6.0% deficiency)	-	15	-	Mostly at interface	-	1	-	Rust from edges spread	-	1
7C-147A ^d 20 (20% t-BuOH)	15	-	-	Mostly at interface & above	10	-	15	Heavy below surface	10	-
8C-147A-20 (20% MeOH)	15	-	-	Mostly at interface & above	10	-	15	Heavy below surface	10	-
11C-147A-20 (20% iso-prop)	15	-	-	Mostly at interface & above	10	-	15	Heavy below surface	10	-
11C-142A-50 (50% iso-prop)	15	-	-	Mostly at interface & above	10	-	15	Heavy below surface	10	-
142A-B ^d + Di-n-Butylamine	20	-	-	Mostly at interface & above	4	-	15	Heavy below surface	4	-
142A-B + Diethylamine	20	-	-	Heavy rust above surface	10	-	15	Heavy rust below surface	10	-
142A-B + Triethylamine	20	-	-	Heavy rust above surface	10	-	15	Heavy rust below surface	10	-
142A-B + Cyclohexylamine	-	20	-	Heavy black rust below surface	-	1/2	-	Few spots on edges	-	15
142A-B + o-Tolyl Thiourea	20	-	-	Heavy rust above surface	10	-	15	Heavy rust below surface	10	-
142A-B + Diethyl Thiourea	20	-	-	Heavy rust above surface	10	-	15	Heavy rust below surface	10	-
142A-B + Diethyl Thiourea	20	-	-	Heavy rust above surface	10	-	15	Heavy rust below surface	10	-
142A-B + Mercaptobenzothiazole	20	-	-	Heavy rust above surface	10	-	15	Heavy rust below surface	10	-
142A-B + Quinoline	20	-	-	Heavy rust above surface	10	-	15	Heavy rust below surface	10	-
142A-B + Purfural	20	-	-	Heavy rust above surface	10	-	15	Heavy rust below surface	10	-
142A-B + Polyoxyethylated alkylamine	20	-	-	Heavy rust above surface	10	-	15	Heavy rust below surface	10	-
142A-B + Ethoxylated alkylolamides	20	-	-	Heavy rust above surface	10	-	15	Heavy rust below surface	10	-
142A-B + Abietylamines (primary)	20	-	-	Heavy rust above surface	10	-	15	Heavy rust below surface	10	-
142A-B + above with 11 moles EO (ethylene oxide) adduct	-	15	-	Heavy rust above surface	10	-	15	Heavy rust below surface	10	-
142A-B + 11 moles adduct & 10% free amine	-	15	-	Heavy rust above surface	10	-	15	Heavy rust below surface	10	-
142A-B + 5 moles adduct & 15% free amine	-	15	-	Less above, more below	10	-	15	Heavy rust below surface	10	-
147A (Glycolic Acid sub for HAC)	0	-	1	Light rust on edges above surface	0	-	0	Heavy rust below surface	0	-
147A (Lactic Acid sub)	0	-	2	Light red rust on area above surface	0	-	0	No visible rust	0	-

^aAdditives were present in amount of 0.5% of external phase or 200 ppm of total emulsion.

^bMetals rated 0-20 as to severity of corrosion.

^cEmulsions 147A, 142A-B, 142A contain 4.0% XP, 37.5% EG, and 0.5, 0.4, 0.3% emulsifier, respectively.

^dEmulsions not otherwise labeled contain 2.2% excess HAC or other acid.

aliphatic acid might prove to be feasible, even though such an acid might have an ionization constant indicating it as a stronger acid than acetic.

One approach was to neutralize the amine with an alkyl phosphoric acid, since many phosphate esters are noted for their corrosion-inhibiting properties. Substitution for acetic acid was attempted with phosphoric acid and complex organic phosphate esters (Emcol CS-136, CS-141, and CS-151 emulsifiers). The neutralizations were performed to a pH of 9.5, which is noncorrosive. However, each time a salt formed that was fairly insoluble in water (HLB of 8-10) and EG, and no satisfactory emulsion with JP-4 would form.

When hydroxy acetic and hydroxy propionic acids (glycolic and lactic acids, respectively) were substituted for acetic acid, the corrosion problem nearly disappeared. No rust was noted for either at a 77°F test temperature exposure (Table XIII), and after 1-week exposure at 140°F the metal coupons showed only minor amounts of rust.

Since the hydroxy acid emulsions were so successful in eliminating corrosion qualitatively, several tests were repeated on a quantitative basis. This time 1- x 3-inch strips of 99-B-613 brass were individually tested in the same emulsions as those used for cold-rolled mild steel.

The metal coupons were cleaned with a nylon brush in water and detergent, dried, and then rinsed in petroleum ether and acetone, respectively. The test was made in duplicate, so that two coupons of each metal were half-immersed in different jars of the same emulsion. These emulsions were then stored for 1 week at 140°F, after which the coupons were rinsed, dried, and reweighed. The weight losses of the individual coupons and the average loss per metal and emulsion are shown in Table XIV.

Again the glycolic and lactic acids caused no significant corrosion of mild steel. Their attack on brass was also much less than that of acetic acid.

Of the two acids (glycolic and lactic), glycolic is the more available at lower cost; it was tested further as an advanced improvement over MEF-1, using a different amine.

9. Emulsifier Improvement

The amine portion of the emulsifier used in MEF-1 emulsion was distilled, hydrogenated tallow primary amine. Distilled tallow primary amine is a mixture of essentially three amines:

TABLE XIV. MILD STEEL AND BRASS CORROSION TESTS - WEIGHT CHANGE MEASUREMENT - METAL COUPONS HALF-IMMERSED												
Acid in Emulsifier	JP-4 as received		Acetic		Acetic		Glycolic		Lactic			
% Acid Excess in Emulsifier	-		4.4		2.2		2.2		2.2			
% External Phase (Wt.)	-		4.14		4.0		4.0		4.0			
% Emulsifier (Wt.)	-		0.4		0.5		0.4		0.4			
% EG in EG/H ₂ O Mixture (Wt.)	-		54.0		37.5		37.5		37.5			
Metal Specimens Tested	JP-4		Steel ^a		Brass ^a		Steel		Brass		Steel	
Weight Change of Metal Coupons (mg) ^b												
Test Specimen #1 ^a	-0.3		-32.9		-21.1		-39.3		-15.5		-0.1	
Test Specimen #2	+0.1		-38.1		-23.6		-29.5		-17.5		-0.7	
Average Weight Change for Each Metal	-0.1		-35.5		-22.4		-34.4		-16.5		-0.4	
^a Mild steel was cold-rolled; brass was 99-B-613.												
^b Metal coupons were 1 x 3 inches; steel was 1/64 inch thick and brass was 1/32 inch thick. The steel coupons weighed 8.7 grams; the brass, 13.3 grams.												
^c Tests were made in duplicate.												

44% oleyl (unsaturated C_{18}), 25% stearyl amine (saturated C_{18}), and 25% palmityl amine (saturated C_{16}). Hydrogenation of the tallow converts all of the oleyl amine to stearyl amine and saturates any of the minor components.

With these reservations in mind, the following three surfactants were tested as possible substitutes for tallow amine:

Surfactant 1 - N-Tallow-1,3-diaminopropane acetate

Surfactant 2 - Dimethyl hydrogenated tallow amine, distilled

Surfactant 3 - Tallow amine

The two amine surfactants were neutralized with an amount of acetic acid based on that required to neutralize tallow amine.

9.1 Surfactant 1

This surfactant was tested in matrix emulsions Nos. 16, 21, and 22. For each, a uniform oil-in-water emulsion was formed. However, when various amounts of acetic acid were added to the No. 16 matrix, normal looking oil-in-water emulsions were formed. But all were of limited stability, as shown in Table XV.

9.2 Surfactant 2

This surfactant was arbitrarily tested in matrix emulsion No. 21, both with and without excess acetic acid. In both, an emulsion was easily produced; but for each, the emulsion started to break after the mixer was stopped (Table XV).

9.3 Surfactant 3

This surfactant was also arbitrarily tested in matrix emulsion No. 21. Only one emulsion was made. It was stable for 6 days at both -30°F and 140°F (Table XV).

This surfactant consists of 90% solids and 10% liquid. The liquid portion was used in the emulsion for the sake of convenience, and it probably represents the oleyl amine portion of the product. Since the liquid portion looked so effective in the preliminary trials, it was tested further as indicated below.

9.4 Oleyl Amine

Which of the primary amines was most beneficial for emulsion preparation and the importance of hydrogenation and distillation had never been determined.

TABLE XV. MATRIX EMULSIONS PREPARED WITH NEW EMULSIFIERS

Emulsion No.	Emulsifier	Emulsifier Weight (g)	Additional HAC (g)	Emulsion Stability*— 1 & 7 Days					
				77°F		140°F		-30°F	
				(1)	(7)	(1)	(7)	(1)	(7)
16	Surfactant 1	4.2	-	X	X	X	X	X	X
16	Surfactant 1	4.2	0.08	X ₁	X ₁	X ₁	X ₁	X ₁	X ₁
16	Surfactant 1	4.2	0.24	+	+	30%	-	+	50%
16	Surfactant 1	3.9	0.30	+	+	50%	-	20%	-
21	Surfactant 1	7.0	-	X	X	X	X	X	X
22	Surfactant 1	7.0	-	X	X	X	X	X	X
21	Surfactant 2	5.8	1.2	X ₁	X ₁	X ₁	X ₁	X ₁	X ₁
21	Surfactant 2	5.6	1.4	X ₁	X ₁	X ₁	X ₁	X ₁	X ₁
21	Surfactant 3 Liquid Portion	5.7	1.3	+	+	+	1%	+	+

*X	-	could not be made
X ₁	-	made, but broke immediately
+	-	stable
%	-	breakdown

Various external phase concentrates were therefore prepared by neutralizing the acetic acid in EG with the following amines: stearyl, oleyl (77%), tall oil (90% oleyl), tallow, distilled tallow, and hydrogenated tallow. Distilled, hydrogenated tallow primary amine was also investigated as a second source material. Four emulsions were prepared with each external phase concentrate (XPC); the stability results are shown in Table XVI and discussed below.

The various amines caused no significant differences in emulsion stability at 140°F. However, the stearyl amine produced two emulsions that were unstable even at 77°F. Stearyl amine and hydrogenated tallow amine produced emulsions that were highly unstable at -30°F, and emulsions containing tall oil or oleyl amine were found to be stable at temperatures as low as -65°F.

Emulsion viscosity at low temperatures was inversely proportional to the amount of unsaturated amine in the emulsifier. Emulsions prepared with oleyl or tall oil amines were much less viscous at -30°F than tallow amine emulsions, and the tallow amine emulsions were much less viscous at -30°F than the hydrogenated tallow amine emulsions were at 0°F. This phenomenon is illustrated in Table XVII, where the yield value of various emulsions is shown first at -16°F and then at 0°F.

9.5 Technical Oleyl Amine From Various Sources

Oleyl amine samples were obtained from various sources for analytical evaluation. The technical grades were usually clear liquids, while the distilled grades were cloudy suspensions that were largely liquid with a small amount of fine solids. Because of this clarity and the significantly lower cost, the technical oleyl amine was preferred over the distilled grade.

The technical oleyl amine samples evaluated included clear liquids, plus a clear sample which also contained some large residual solids (filterable). Two gallons of amine was purchased for future emulsion preparations, and a sample of this was also analyzed. A distilled sample of oleyl amine was included for comparison.

The five amine samples were dissolved in acetic acid and titrated electrometrically with 0.02 normal perchloric acid. From the amount of titrant required were calculated the amount of required glycolic acid, the amine number of the sample (milligrams KOH per gram of amine), and the average molecular weight. The results of these calculations are shown in Table XVIII, and the methods of calculation are:

TABLE XVI. EMULSIFIER AMINE SUBSTITUTION - EFFECT ON EMULSION STABILITY												
Total External Phase (%)	4.0			4.0			4.0			4.0		
% EG/H ₂ O	37.5			37.5			37.5			50.0		
% Emulsifier	0.5			0.5			0.4			0.4		
% Excess Acetic Acid	2.2			2.2			2.2			2.2		
Stability; 7 Days at:	77°F	140°F	-30°F	77°F	140°F	-30°F	77°F	140°F	-30°F	77°F	140°F	-30°F
Amine Substitute for Hydrogenated Tallow Amine, Distilled	+	1%	+	+	Syn	+	+	1%	+	+	3%	+
Technical Oleyl Amine	+	3%	+	+	Syn	+	+	2%	+	+	3%	+
Technical Tall Oil Amine	+	1%	80%	1%	2%	70%	Syn	1%	70%	+	Syn	50%
Technical Stearyl Amine	+	Syn	+	+	2%	+	+	2%	+	+	3%	+
Tallow Amine, Distilled	+	+	+	+	1%	+	+	1%	+	+	3%	+
Technical Tallow Amine	+	Syn	20%	+	1%	10%	+	Syn	10%	+	2%	50%
Hydrogenated Tallow Amine	+	Syn	1%	+	Syn	+	+	1%	15%	+	2%	20%
Hydrogenated Tallow Amine, Distilled	+	Syn	1%	+	Syn	+	+	1%	15%	+	2%	20%
<div>+ = Stable</div> <div>Syn = Syneresis</div> <div>% Values = JP-4 separation</div>												

+ = Stable
 Syn = Syneresis
 % Values = JP-4 separation

TABLE XVII. EMULSIFIER AMINE SUBSTITUTION - EFFECT ON LOW-TEMPERATURE EMULSION VISCOSITY									
Yield Values, dynes/cm ²									
	Amine Substitute							Hydrogenated Tallow, Distilled	
	Oleyl	Tall Oil	Stearyl	Distilled Tallow	Technical Tallow	Hydrogenated Tallow			
Emulsion Age	10 Days	9 Days	9 Days	9 Days	8 Days	7 Days	7 Days		
Yield Value at 77°F	880	780	930	850	960	1000	970		
7-Day-Old Emulsions, plus 1 Day at -16°F									
Yield Value at -16°F	1350	1000		3450					
Above Emulsions, 3 More Days at -16°F, Then 3 Days at 0°F									
Yield Value at 0°F	1400	1190		2700			8200*		
*Several hours old, then 1 day at 0°F.									
% Total XP - 4.0									
% EG/H ₂ O - 37.5									
% Emulsifier - 0.5									
% Excess Acetic Acid- 2.2									

TABLE XVIII. AMINE CONTENT IN TECHNICAL OLEYL AMINES FROM VARIOUS SOURCES					
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Grade	Technical	Technical	Technical	Technical	Distilled Tall Oil
Physical Appearance	Clear liquid	Clear liquid	Clear liquid	Clear liquid with solid chips on bottom	Cloudy liquid with small percentage of settling sludge
Titration Results; mg KOH/g Amine					
Amine No.	209	209	205	206	201
Average Molecular Weight	268	268	274	272	279
Grams Glycolic Acid per Gram of Amine	0.2834	0.2834	0.2777	0.2791	0.2723
% Glycolic Acid in Stoichiometric Emulsifier	22.08	22.08	21.73	21.90	21.40

- Grams of glycolic acid/gram of amine =
 milliliters x normality (titrant) x 0.076 (1)
- % Glycolic acid in emulsifier = $[(1)/(1)+1] \times 100$ (2)
- Amine number = (1) x 56,100/76.05 (3)
- Average molecular weight = grams of sample x
 100/milliliters x normality (titrant) (4)

9.6 Oleyl Amine MEF-2 Emulsion Preparation

Gallon quantities of six MEF-2 candidate emulsions were prepared with the Hobart Model C-100 mixer so that physical properties could be determined. Each emulsion had 4.0% external phase and contained an emulsifier of technical oleyl amine neutralized with either acetic, glycolic, or lactic acid. Two emulsions were prepared with each emulsifier acid and contained an EG/water ratio of either 37.5% or 28.6%. The 37.5% ratio is that of MEF-1, while 28.6% was arbitrarily chosen because it coincides to a 2/1 ratio of EG and emulsifier, that of the standard XPC.

The emulsions were prepared by the standard procedure, and it was then noticed that the corresponding emulsions with glycolic and lactic acids were of greater volume than those with acetic acid. More evident was the greater volume of the emulsions with 28.6% EG versus 37.5%. This phenomenon indicates a difference in the amount of air entrapped during mixing, and the suspicion was confirmed later with the microscope. Entrapped air may not be a problem in a completely enclosed mixing system.

Since corrosion reduction is a desired objective, comparative tests were made with acetic, glycolic, and lactic acids and with oleyl amine.

One- by three-inch mild steel and brass coupons were cleaned with water and detergent, rinsed successively in petroleum ether and acetone, and weighed gravimetrically. Two coupons of each material were individually half-immersed in 4-ounce jars of each emulsion, and the jars were then stored 1 week at 140°F. After this time, the coupons were again rinsed and reweighed. The weight losses are shown in Table XIX (see also Table XIV).

Severe corrosion occurred on the mild steel panels in both acetic acid emulsions, but none was visually detected on those panels in the lactic and glycolic acid emulsions. The former coupons lost significantly in weight while the latter coupons gained slightly in weight. The variation in EG/water ratio seemed to have no significant effect on the amount of steel or brass corrosion.

TABLE XIX. MEP-2 CANDIDATE EMULSIONS - MILD STEEL AND BRASS CORROSION WEIGHT CHANGE MEASUREMENT - METAL COUPONS HALF-IMMERSED													
% External Phase	4.0		4.0		4.0		4.0		4.0		4.0		4.0
Acid in Emulsifier ^a	Acetic		Acetic		Glycolic		Glycolic		Glycolic		Lactic		Lactic
% Emulsifier	0.5		0.5		0.5		0.5		0.5		0.5		0.5
% EG in EG/H ₂ O Mixture	37.5		28.6		37.5		28.6		37.5		28.6		28.6
Metal Tested ^b	Steel		Brass		Steel		Brass		Steel		Brass		Brass
Weight Change of Metal (mg)													
Test Specimen #1	-4.4	-15.0	-27.6	-16.3	+0.7	-6.6	+0.9	-6.6	+1.5	-9.1	+1.9	-8.1	
Test Specimen #2	-37.5	-17.6	-29.0	-19.0	+0.6	-6.3	+0.5	-6.6	+2.2	-10.0	+1.8	-9.8	
Average Weight Loss for Each Metal	-39.0	-16.3	-28.3	-17.6	+0.6	-6.4	+0.7	-6.6	+1.7	-9.5	+1.8	-8.9	

^a Emulsifier contains oleyl amine neutralized with particular acid, an amount equal to 1% less stoichiometry.

^b Metal coupons tested were 1 x 3 in. hes; steel was 1/64-inch-thick cold-rolled and brass was 1/32-inch-thick 99-B-613.

The switch to lactic acid from acetic acid reduced the brass corrosion by a factor of two, while switching to glycolic acid reduced the corrosion by a factor of three.

9.7 Cloud and Freezing Points of MEF-2 External Phase Concentrate (XPC)

MEF-2 XPC containing a 2:1 ratio of EG and emulsifier, plus a small amount of water from the glycolic acid, was checked for cloud point and freezing temperature. A test tube containing the XPC and a thermometer was inserted into a Dewar flask containing methanol. Dry ice was added gradually to the methanol in order to slowly lower the temperature of the XPC. At 5°F the emulsifier began to precipitate from the glycol solution, which then became very stiff. When the XPC was allowed to warm up again, the solution became clear at about 10°F.

When 10% of the water necessary for an emulsion was added to the XPC, the emulsifier began to precipitate at 20°F, and the solution again became stiff at 5°F. When allowed to warm up, the XPC became clear at 30°F.

The XPC appears to have a low enough freezing point for easy handling at low temperatures. The solubility of the emulsifier in the JP-4 phase is no doubt the limiting factor in low-temperature emulsion preparation. Emulsions have been prepared with 40°F JP-4, but the process was slower than with 77°F fuel.

10. Emulsifier Stoichiometry

Excess amine is soluble in JP-4, but excess acid may be the cause for considerable corrosion. Consequently, XPC's were prepared which contained amounts of glycolic acid at stoichiometric, 1% less than stoichiometric, and 2% greater. The XPC with acid deficiency was prepared with solid reagent grade glycolic acid, while the other two were prepared with the commercial acid solution. Emulsions were prepared in the Hobart mixer, and their relative stability, pH, and mild steel corrosion properties were determined. The results are shown in Table XX.

10.1 Mild Steel Corrosion

One- by three-inch strips of cold-rolled mild steel were cleaned with detergent and water and successively rinsed in petroleum ether and acetone. The metal coupons were weighed and then half-immersed in two jars each of the various emulsions. After storage for 1 week at 140°F, the coupons were removed from the jars; rinsed in water, petroleum ether, and acetone; and reweighed. The average weight loss of mild steel

in each emulsion was determined and is shown in Table XX. The amount of corrosion on all of the coupons was insignificant, and none could be detected visually.

TABLE XX. EMULSIFIER ACID CONTENT EFFECT ON CORROSION, pH, AND STABILITY			
% External Phase	4.0	4.0	4.0
% Emulsifier	0.5	0.5	0.5
EG/H ₂ O Ratio	37.5	37.5	37.5
Acid Above Stoichiometry	-1%	0	2%
Mild Steel Corrosion, 7 days of half immersion at 140°F; average weight loss per coupon, mg	0.2	0.1	0.4
Emulsion pH	4.9	4.6	4.5
Emulsion Stability, 7 days at 140°F (% JP-4), % free JP-4	1%	3%	2%

10.2 Emulsion pH

Calomel and glass electrodes attached to a Beckman pH meter were immersed in the three emulsions. Because the emulsions are not true liquids and contain entrapped air, the meter readings were unsteady. However, the readings obtained most consistently were considered true and are shown in Table XX.

The pH readings of the MEF-2 emulsions were about one unit less than those for the MEF-1 emulsions; this is consistent with the fact that glycolic acid is 9.4 times stronger than acetic acid.

10.3 Emulsion Stability

Half-filled quart jars of each emulsion were stored 1 week at 140°F. At the end of this time, each jar contained only a small amount of JP-4 as a result of either evaporation-condensation or slight emulsion instability. The relative amounts of JP-4 are shown in Table XX as total percentages; however, the absolute differences are small enough to be due to experimental error.

In summary, these small differences in glycolic acid content failed to show marked differences in corrosion, pH, or emulsion stability. As might be expected, the -1% acid resulted in higher pH (excess amine), but the changes other than this were minimal.

11. MEF-2 Formula Selection

The tests cited above show that switching from acetic acid to a hydroxy acid greatly reduced or nearly eliminated the corrosion problem, while switching from tallow amine to either oleyl amine or tall oil amine practically eliminated the low-temperature stability and viscosity problems. Thus, the MEF-1 formulation with emulsifier containing one of these acids and amines is the likely MEF-2 emulsion preference.

Tests showed that excess acid or amine in the emulsifier did not improve the performance of the emulsion. Therefore, stoichiometry should be the goal, to prepare the emulsifier for maximum effectiveness. It is unlikely that any emulsion would contain exact quantities of acid and amine because of limitations of commercial weighing equipment. Since glycolic acid is the minor component in the emulsifier (22%), a small excess would result in a loss of amine glycolate equal to only two-ninths of the excess acid. However, a deficiency in acid would result in a loss of amine glycolate equal to the entire amount. Therefore, a goal of 1% excess acid in the emulsifier is recommended to more nearly achieve stoichiometry.

To compare the acetic acid formulation of oleyl amine with the formulations comprising hydroxy acids, a series of parallel tests was made to determine droplet size, yield value, and thermal stability.

The yield values were determined for all emulsions shortly after preparation. The method used was the now-standard procedure with the modified ASTM cone penetrometer cited in Appendix II.

A full 1-quart jar of each emulsion was stored for 30 days at 140°F; a leveled, covered, 800-milliliter Griffin beaker of emulsion was stored at -30°F; and a full half-gallon jar was stored at 77°F. Then, the yield value was again determined at 77°F for the 140°F and 77°F stored emulsions; it was also determined at 0°F for the -30°F stored emulsions, both before and after the 30-day period.

The results in Table XXI show that the emulsions with acetic acid are slightly more viscous initially. The differences in yield value become negligible, however, after the 30-day

TABLE XXI. MEF- CANDIDATE EMULSIONS - DROPLET SIZE, YIELD VALUE, AND STABILITY TESTS						
Acid Used to Neutralize Oleyl Amine in Emulsifier		Acetic	Acetic	Glycolic	Glycolic	Lactic
Total External Inase %		4.0	4.0	4.0	4.0	4.0
EG/H ₂ O Ratio; % EG		37.5	28.6	37.5	28.6	37.5
% EG of Total Emulsion		1.31	1.00	1.31	1.00	1.31
% H ₂ O of Total Emulsion		2.19	2.50	2.19	2.50	2.19
% Emulsifier in Emulsion		0.5	0.5	0.5	0.5	0.5
Droplet Size (μ)						
Range		2-7	1-8	2-7	1-9	2-8
Median Size		3	5 ^a	3	5	5
Yield Value (dynes/cm ²)						
Test Temp.						
77°F		1630	1400	1390	1250	1210 ^b
50°F		1760	1570	1380	1220	1400
0°F		1280	1470	1020	1080	1200
77°F		750	750	750	750	620
77°F		450	410	480	590	480
Thermal Stability						
Days						
30		+	+	+	+	+
30		+	+	+	+	+
30		5% ^c	5% ^c	2%	2%	2%

^a Hobart mixer entrapped more air in all 28% EG emulsions which produced less-efficient mixing.

^b This emulsion sat 1 hour before yield value was determined.

^c These two emulsions had turned a dark yellow-brown color after 30 days, starting at 20. % values indicate estimated free fuel.

storage periods. No significant difference was noted between corresponding emulsions with the different EG/water ratios.

All the emulsions were stable for 30 days at both 77°F and -30°F, and all contained minor amounts of free JP-4 after 30 days at 140°F. The emulsions with acetic acid definitely contained more free liquid than the glycolic and lactic acid emulsions (about 5% vs 2%). In addition, both acetic acid emulsions had turned dark yellowish-brown, while the other emulsions contained only a slight amount of yellowness near the top of the jar. The small amount of JP-4 that breaks out of every emulsion during storage at 140°F suggests an evaporation-condensation cycle rather than emulsion instability.

Again, there were no differences in thermal stability between like emulsions with the different EG/water ratios.

Droplet size range and median value were determined (via the microscope) for the six emulsions on the day of preparation. The type of acid had no effect on droplet size, while the EG/water ratio made a noticeable difference. All the emulsions with 28.6% EG/water contained more entrapped air and had a higher median value droplet size. It is believed that the greater amount of entrapped air reduced the mixing efficiency and resulted in larger droplet size.

Since the parameters of 4.0% external phase, 0.5% emulsifier, and 37.5% EG/water were optimum for MEF-1, they were also adopted for the preliminary MEF-2 formulation. Confirmatory tests were run in the form of a limited matrix evaluation. Emulsifier content was varied from 0.3% to 0.7%, while the EG/water ratio was varied from 28.6% to 75.0% EG.

An external phase concentrate of 2:1 EG:emulsifier ratio was maintained with 1% excess glycolic acid.

An advantage of the oleyl amine glycolate formulation over MEF-1 is that no additional heating of the external phase is required for emulsion preparation. Both commercial glycolic acid and technical oleyl amine are clear liquids at 77°F, and their salt remains liquid after formation in the ethylene glycol.

A reason for maintaining the ethylene glycol at a higher ratio is its excellent solvency for oleyl amine glycolate. This emulsifier has shown a preferential solubility in the water-EG phase over JP-4 when an emulsion is broken by high shear. Since the glycolate is not too soluble in water alone, a reduction in the amount of EG below 28% might alter this preferential solubility.

Seven-hundred-gram quantities of emulsion containing variable amounts of external phase components were then prepared in the Hobart Model C-100 mixer. Two emulsions of each formulation were made, and 7-day 140°F stability tests were run. The average results and emulsion parameters are shown in Table XXII.

The results confirm that emulsion formulation 4 is optimal for MEF-2. Although formulation 3 is equal in thermal stability, it has the disadvantages of more easily absorbing air during preparation and passing initially through a more chunky stage. The stabilities of the matrix emulsions adjacent to 4 show that moderate deviations of MEF-2 components should not adversely affect emulsion performance.

These data demonstrate that the preferred formulation, as with MEF-1, is a 4% external phase, 0.5% emulsifier containing 1% excess acid and a 37.5/62.5 EG/water ratio.

MEF-2 PROPERTIES

12. Yield Stress Change With Age

A 2800-gram quantity of MEF-2 emulsion was prepared in the Hobart Model C-100 mixer. The yield stress was measured immediately, weekly during the first month of storage at 77°F, and again after 60 and 90 days of total storage. There was no free JP-4 or other sign of emulsion deterioration at the 90-day measurement. The results are given in Table XXIII and are shown graphically in Figure 1.

As the large drop in viscosity after the first week was probably due to loss of entrapped air incurred during the mixing process, the specific gravity change with time was determined.

13. Specific Gravity Change With Time

The specific gravity was determined for freshly prepared MEF-2 emulsion and also for 10-week-old emulsion. Both emulsions had been prepared in the Hobart Model C-100 mixer.

A 1-liter graduated cylinder terminated at the 570-milliliter mark was used as the weighing container. It was weighed empty and also when full of either water or one of the specific emulsions.

The water was poured into the cylinder until its surface coincided to that of the plane of the cylinder top. The emulsions were spooned into the cylinder, and any excess was removed with

TABLE XXII. MATRIX FORMULATION STABILITIES				
Emulsion No.	% External Phase	% Emulsifier	% EG/H ₂ O	Average % JP-4 Separation @ 140°F
1	4.0	0.3	37.5	5
2	4.0	0.4	37.5	1
3	4.0	0.5	28.6	Syneresis*
4	4.0	0.5	37.5	Syneresis
5	4.0	0.5	50.0	1
6	4.0	0.5	75.0	100
7	4.0	0.6	37.5	1
8	4.0	0.7	37.5	5
*Formation of JP-4 droplets				

TABLE XXIII. YIELD STRESS CHANGE WITH AGE	
Period of 77°F Storage	Yield Stress (dynes/cm ²)
Immediately	1420
1 week	910
2 weeks	870
3 weeks	790
1 month	750
2 months	690
3 months	690

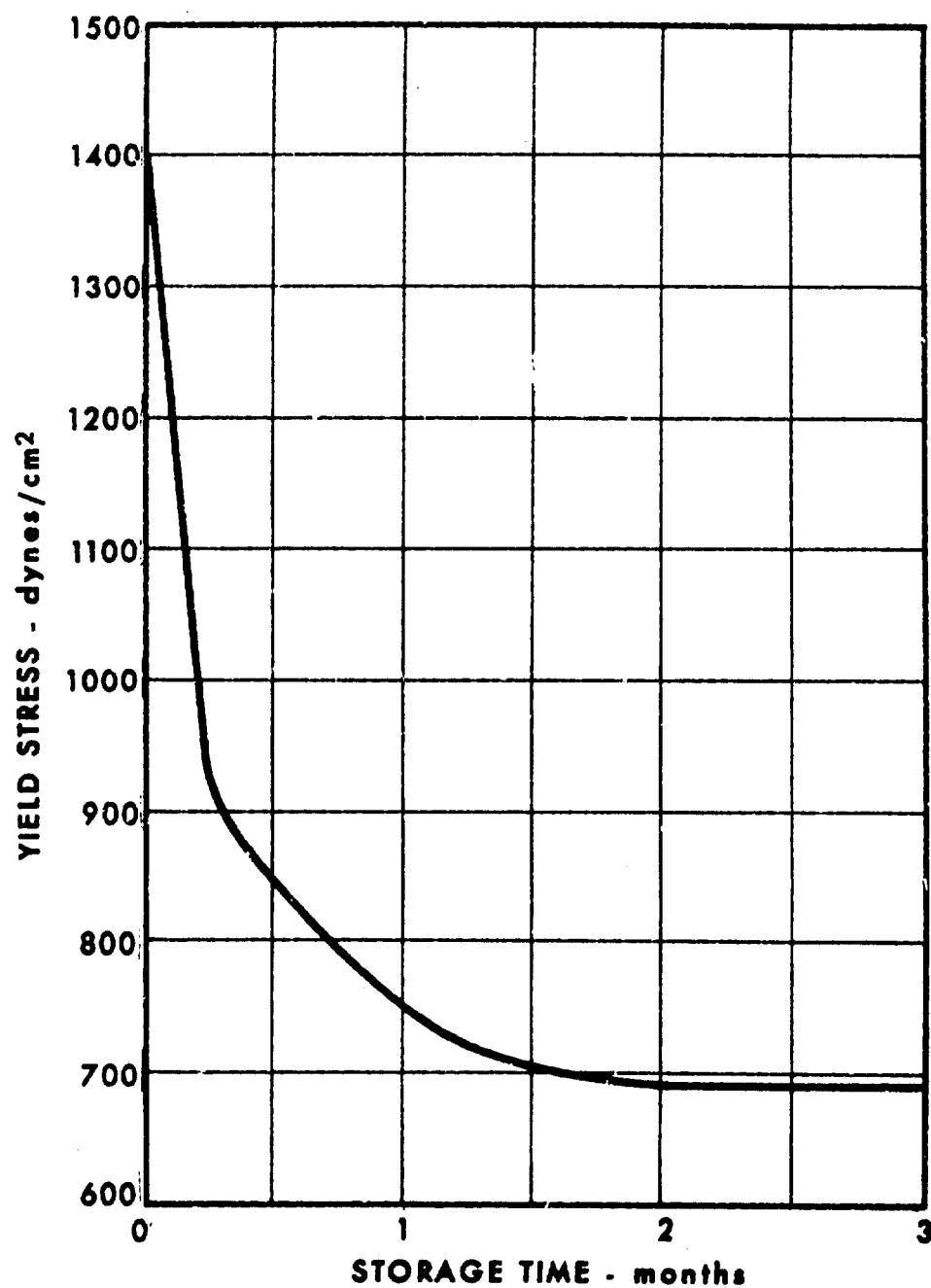


Figure 1. Yield Stress Change With Age of MEF-2 Emulsion at 77°F.

a straightedge. Any large pockets of air had been previously pulled out by the action of a spatula. The cylinder was filled and weighed three times for each of the test fluids; an average weight was used to determine the specific gravities.

At the conclusion of the specific gravity determinations, the yield stress was measured for the two emulsions. The results are shown in Table XXIV.

The difference in specific gravities shows that loss of entrapped air is the best explanation for the lowering of yield stress in aged emulsions.

TABLE XXIV. SPECIFIC GRAVITY CHANGE WITH AGE			
Fluid	Age	Specific Gravity	Yield Stress (dynes/cm ²)
Water	-	1.00	-
MEF-2	2 hrs	0.665 ± 0.001	1050
MEF-2	10 wks	0.731 ± 0.001	780

14. Emulsion Solubility

It is already known that chemical demulsification by releasing the amine results in an almost quantitative removal of the amine to the recovered JP-4 phase. The objective of this experiment was to show the relative solubility of the MEF-2 emulsifier in the JP-4 either in the emulsion condition or broken from the emulsion by shear.

The experimental details follow. About 100 ml of C¹⁴-labeled MEF-2 was treated for 5 minutes in a blade blender. The resulting partially broken emulsion (~50%) was then centrifuged for 5 minutes at 500 g in a clinical centrifuge. Duplicate 1-gram samples of the clear JP-4 were removed, and the radioactivity was measured with a Tri-Carb Scintillation Spectrometer. The above procedure was repeated twice.

The partition coefficient is defined as the concentration of emulsifier in 1 gram of fuel divided by the concentration in 1 gram of external phase. Knowing the original activity in the emulsion (cpm/g), and having measured the activity in 1 gram of the recovered JP-4, the activity is determined in 1 gram of external phase, by difference.

Knowing the partition coefficient, we can then determine the percentage of emulsifier dissolved in the JP-4 from the following equation:

$$\% = \frac{100 \times \text{Partition coefficient}}{\text{Partition coefficient} + \text{grams XP/grams JP-4}} \quad (5)$$

Multiplication of the above percent by the original emulsifier concentration of 0.005 then yields the actual emulsifier concentration in the recovered JP-4. The results are shown in Table XXV.

The results show that nearly all (99.7%) of the released emulsifier has preferentially dissolved in the water-EG phase.

14.1 C¹⁴-Labeled Glycolic Acid

A 700-gram quantity of MEF-2 was prepared with C¹⁴-labeled glycolic acid. Two 100-milliliter quantities of this emulsion were treated for 5 minutes in a blade blender. The resulting partially broken emulsions (~50%) were then centrifuged for 5 minutes at 500 g in a clinical centrifuge. Duplicate 1-gram samples of the clear JP-4 were removed from each container, and the radioactivity was again measured with a Tri-Carb Scintillation Spectrometer.

The two samples of partially broken emulsion were then stored at 77°F in the stoppered centrifuge containers. Duplicate 1-gram samples of the clear JP-4 were again withdrawn after three consecutive 30-day periods, and the radioactivity was measured.

The results show that the partition coefficient remains essentially constant (within experimental significance) during 90 days of storage (Table XXV). Only about 0.3% of the glycolic acid emulsifier remains in the JP-4 recovered by shear. This is equivalent to an absolute concentration in the JP-4 of 0.002%.

14.2 Oleyl Amine Titration

The above tests with C¹⁴-labeled glycolic acid were run with the expectation that the oleyl amine part of the emulsifier would remain connected to the glycolic acid after shear breakdown of the emulsion. However, the monitoring of radioactivity in broken emulsion is really only a measurement of the glycolic acid alone. Therefore, an amine determination was also run on the recovered JP-4 after completion of the 90-day storage and all radioactivity measurements.

TABLE XXV. CONCENTRATION OF C ¹⁴ -LABELED GLYCOLIC ACID IN RECOVERED JP-4 C ¹⁴ -Labeled MEF-2 was 50% Broken by Shear and Stored at 77°F							
Emulsion No.	Sample No.	Broken Emulsion Stored (days)	Initial Emulsion Activity (cpm/g)	Recovered JP-4 Activity (cpm/g)	Partition Coefficient	Fractional Wt % of Total Emulsifier in JP-4	Actual Emulsifier Concentration in JP-4 (wt %)
1	a	0	256,585	977	1.53×10^{-4}	0.366	0.0018
	b	"	"	983	1.54×10^{-4}	0.368	0.0018
2	a	"	"	755	1.18×10^{-4}	0.282	0.0014
	b	"	"	806	1.26×10^{-4}	0.302	0.0015
1	a	30	"	842	1.32×10^{-4}	0.315	0.0016
	b	"	"	815	1.27×10^{-4}	0.305	0.0015
2	a	"	"	757	1.18×10^{-4}	0.283	0.0014
	b	"	"	750	1.17×10^{-4}	0.281	0.0014
1	a	60	"	943	1.48×10^{-4}	0.353	0.0018
	b	"	"	968	1.52×10^{-4}	0.362	0.0018
2	a	"	"	886	1.39×10^{-4}	0.332	0.0017
	b	"	"	901	1.41×10^{-4}	0.337	0.0017
1	a	90	"	1145	1.79×10^{-4}	0.429	0.0021
	b	"	"	1109	1.74×10^{-4}	0.415	0.0021
2	a	"	"	1088	1.70×10^{-4}	0.407	0.0020
	b	"	"	1118	1.75×10^{-4}	0.418	0.0021

The standard nonaqueous titration procedure was used whereby 10 milliliters of the JP-4 was dissolved in glacial acetic acid and then titrated with 0.02N perchloric acid and crystal violet indicator. JP-4 from both broken emulsions was titrated, and the results are shown in Table XXVI.

TABLE XXVI. OLEYL AMINE SOLUBILITY			
JP-4 Source, Emulsion No.	Grams Amine per 100 ml of JP-4	Wt % of Amine in JP-4 Phase	% Concentration of Amine in JP-4
1	0.0160	5.3	0.0207
2	0.0128	4.3	0.0166

Surprisingly, the amount of amine found was ten times larger than that indicated by the glycolic acid tests. However, a range of 2-4% of the initial oleyl amine has consistently been found in the recovered JP-4 from all types of high shear equipment.

It appears from the above tests that high-shear-recovered JP-4 will contain 10 parts of oleyl amine for every 1 part of glycolic acid, or it will contain a concentration of approximately 0.02% oleyl amine and 0.002% glycolic acid.

In the separated JP-4, the glycolic acid will be present as amine glycolate, and 9 out of 10 parts of the oleyl amine will essentially be in the free state. Apparently, the preferential solubility attraction for EG and water of the other 9 parts of glycolic acid is stronger than for the weak chemical bond between the amine and glycolic acid.

An interesting confirmatory test would have been to break an emulsion containing C¹⁴-labeled oleyl amine and then perform the series of radioactivity measurements. However, a source of radioactive oleyl amine was not found.

15. Droplet Size Variation With Age

Five gallons of MEF-2 emulsion was prepared with the Hobart Model C-100 mixer and stored in a 5-gallon jar. Three 4480-gram batches (1.7 gallons) were prepared by slowly adding all the JP-4 to the external phase and mixing the emulsion for 8 minutes after the last fuel addition (#2 speed). Emulsion

from each batch was examined under the microscope for droplet size range and median value. The values were similar to those of MEF-1.

Samples were again drawn from depths of 2, 8, and 15 inches by application of vacuum to a 1/4-inch glass tube. The droplet size range and median value were measured under the microscope, and a complete summary of results over the 2-month period is shown in Table XXVII.

TABLE XXVII. DROPLET SIZE VARIATION WITH AGE						
Sampling Depth Droplet Size	2" (Top)		8" (Middle)		15" (Bottom)	
	Range	Median	Range	Median	Range	Median
Initially	1-7 μ	5 μ	2-5 μ	5 μ	2-8 μ	5 μ
30 days	2-10	6	2-7	4	2-7	4
60 days	3-10	6	2-8	5	2-6	4

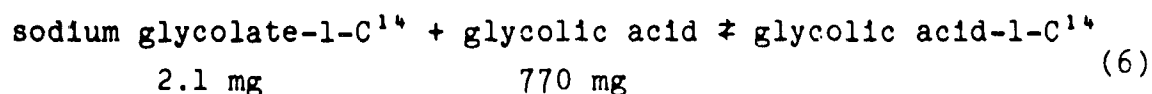
The results show that emulsion droplet size stays essentially constant during long-term storage at 77°F. The emulsion near the top may have undergone a slight amount of droplet coalescence due to suspected evaporation and condensation of the JP-4.

The results also show that change in droplet size is not the reason for the yield stress drop of the emulsion after preparation.

16. Emulsifier Migration

16.1 Radiotracer Technique

To study the migration of emulsifier in MEF-2 during centrifugation, about 700 grams of emulsion was prepared containing C^{14} -labeled oleyl amine glycolate. To a mixture of 14.90 grams water, 9.180 grams ethylene glycol, and 1.228 grams glycolic acid (MCB, 64.4%) was added 0.1 mc (2.1 mg) of sodium glycolate- $l-C^{14}$ (46.9 μ c/mg). It was assumed that the following equilibrium was rapidly established:



and that >>99% of the activity was converted to glycolic acid-1-C¹⁴. Finally, 2.722 grams of oleyl amine was added and the mixture was stirred. The emulsion was prepared from 902 ml of JP-4 in a Hobart mixer in the usual manner.

The initial activity of the emulsion was measured. Three samples (~1.5 grams each) were weighed into polyethylene vials and were treated with 10.1 ml of dioxane "cocktail". The samples were counted in a Packard Model 3003 Tri-Carb Scintillation Spectrometer. The average activity was 256,585 cpm/g.

16.2 Centrifugation

Duplicate 100-ml portions of the emulsion were centrifuged for 5 days at 500 g in an International Centrifuge, Model V (auto-transformer setting 18). At 24-hour intervals, the centrifugation was interrupted and duplicate 1.5-gram samples were removed from each centrifuge tube at a depth 1 inch from the top surface (Zone 2 of Figure 2); the samples were counted as described above. Results, presented in Table XXVIII and Figure 3, provide a quantitative measurement of the migration of the emulsifier as a function of time.

TABLE XXVIII. EMULSIFIER MIGRATION - 500 g's Effect of Centrifugation on MEF-2				
Time (Days)	Average Activity (cpm/g)		Mean Activity (cpm/g)	% of Initial Activity
	Sample 1	Sample 2		
0			256,585	
1	254,039	255,217	254,628	99.2
2	246,921	252,362	249,642	97.3
3	238,163	241,426	239,820	93.5
4	221,261	225,795	223,528	87.1
5	213,494	217,151	215,323	83.9

Less than 1% decrease in concentration of emulsifier was noted after the first day. However, increasing losses were found after the second, third, and fourth days. Finally, after the fifth day, a total of 16% of the emulsifier had migrated beyond a depth of 1 inch from the surface of the emulsion.

Figure 2 shows visual changes which occurred after 5 days. That Zone 1 is clear is explained by reduction in external phase and emulsified air. Zone 2 was the 1-inch sampling point. Zone 3, though quite turbid, was lower in emulsifier than the zone immediately above. Zone 4 was comprised of ethylene glycol, water, and about 15% of the total initial emulsifier.

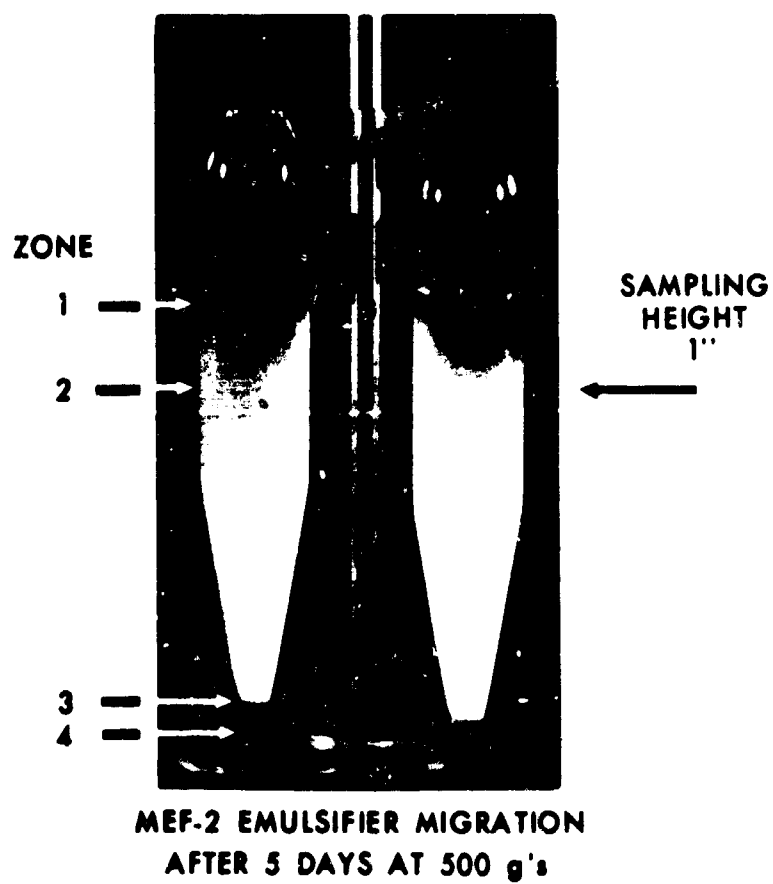


Figure 2. Centrifuged MEF-2.

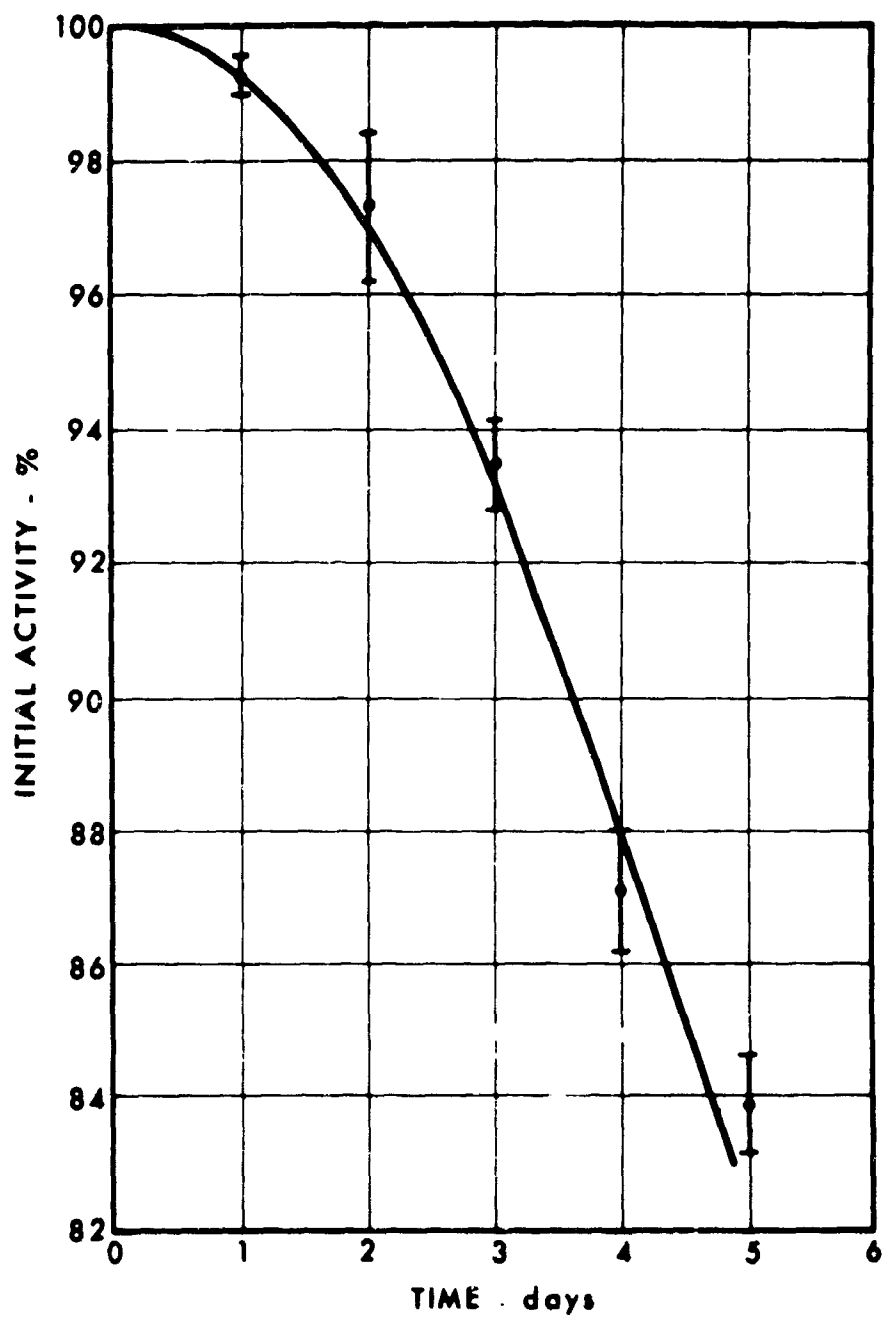


Figure 3. Migration of Emulsifier - Activity as a Function of Time at 500 g's.

16.3 Emulsion Appearance

After the first day, a transparent zone extending to a depth approximately 1/2 inch from the top of the emulsion was observed. This zone did not increase in length during the remaining 4 days of the test.

Sampling of this zone after the fifth day yielded activities corresponding to 74.7% of the initial activity of the emulsion. It is important to note that, with the exception of the small amount of the external phase separation described below, the emulsion did not break during the 5-day test. There was no evidence of free fuel even at the top surface of the emulsion, where the emulsifier concentration had been reduced to 75% of its initial 0.5% value.

Separation of a second, heavier phase, which increased in volume each day, was noted. After days 1 through 5, the volumes were 0.05 ml, 0.10 ml, 0.25 ml, 0.40 ml, and 0.50 ml, respectively. After the fifth day, infrared spectrophotometric analysis indicated that the phase consisted of water and ethylene glycol. A significant amount of emulsifier was also present, as indicated by activities of 5.2×10^6 and 4.7×10^6 cpm/g. These levels of activity are equivalent to ~60 mg of emulsifier in the 0.5 gram of water-glycol, or about 15% of the total initial activity.

In the emulsion zone immediately above the water-glycol phase, increased turbidity was noted. This area was sampled after the fifth day and yielded values of 231,000 and 180,000 cpm/g in samples 1 and 2, respectively. Because of loss of activity in the top zone of the emulsion, and very high activity in the external phase, this zone might be expected to yield activities corresponding to high concentrations of emulsifier. The levels, however, correspond to an emulsifier concentration significantly less than the initial activity. The observation can perhaps be explained by increased tendency of the emulsifier to partition into the free water-glycol phase in the emulsion zone immediately adjacent to the water-glycol phase.

16.4 Emulsifier Migration at 140°F

An 8-ounce jar was three-fourths filled with C¹⁴-labeled MEF-2 and stored 30 days at 140°F. One-gram samples were then removed from the very top, middle, and bottom of the jar for radioactivity measurement with the Tri-Carb Scintillation Spectrometer.

The emulsion at the bottom and middle of the jar had nearly identical radiation levels, while that at the very top had a

level only 93% as intense. These results show that there is essentially no emulsifier migration even at this temperature.

The top emulsion probably had less activity per gram because of JP-4 dilution, resulting from evaporation and condensation.

17. Agitation After Aging

MEF-2 emulsion stored 90 days at 77°F (in a 5-gallon jar) was used for this experiment. The yield stress was measured, and then part of the emulsion was pumped either through a gear pump or a centrifugal pump. The gear pump operated at 1800 rpm at about 5 gpm, while the centrifugal pump operated at 3500 rpm and produced about 17 gpm. After a single pass through the pumps, the yield stress was again measured; the results are shown in Table XXIX. The centrifugal pump had a much more violent action than the gear pump, as was shown by the larger increase in yield stress.

TABLE XXIX. AGITATION AFTER AGING			
Emulsion Condition	90-day storage	After gear pump	After centrifugal pump
Yield Stress	630 dynes/cm ²	660 dynes/cm ²	780 dynes/cm ²

18. Thermal Conductivity

Thermal conductivity (the amount of heat passing in unit time through a unit volume of a substance when its opposite faces differ by 1 degree) was determined at 25° ± 2°C for JP-4 and 14-day-old MEF-2 emulsion. The method used was the hot wire technique, whereby a thin wire is mounted in the center of a cylinder containing the test fluid and its resistance is measured as a function of applied electric heating current. The resistance and temperature of the heated wire will be inversely proportional to the thermal conductivity of the surrounding test fluid, according to the following relationship:

$$K = \frac{1}{2\pi L} \left(\frac{I^2 R}{T_1 - T_2} \right) \ln \frac{R_1}{R_2} \quad (7)$$

where K = thermal conductivity, cal/sec cm °C

L = length of wire, cm

I = current passed through wire, amps

R = wire resistance, ohm

T₃ = heated wire temperature, °C

T₀ = bath temperature or initial wire temperature, °C

R₀ = wire radius, cm

R₁ = liquid cylinder radius, cm

For our test apparatus, the equation reduces to

$$K = \frac{AI^2R}{T_3 - T_0} \quad (8)$$

where A is a proportionality constant. Since temperature change is proportional to resistance change,

$$T_3 - T_0 = \Delta T = B\Delta R \quad (9)$$

$$\text{and } K = \frac{AI^2R}{B\Delta R} = \frac{CI^2R}{\Delta R} = \frac{CI^2}{\Delta R/R} \quad (10)$$

where A, B, and C are constants.

In order to determine the value of C for our apparatus, a reference liquid was tested for which the thermal conductivity was already known: in this case, reagent grade toluene. J. K. Horrocks and E. McLaughlin¹ reported the thermal conductivity of toluene at 25°C to be 318×10^{-6} cal/sec cm °C. Various amounts of current were passed through the wire immersed in toluene, and each time wire resistance was measured. The percentage change in resistance $\Delta R/R$ was plotted against I^2 , and the best-fitting part of this curve was extrapolated to zero. The inverse of the slope of the resulting line (Figure 4) was then considered to be equal to the term $I^2/\Delta R/R$; therefore,

$$C = \frac{K_{\text{toluene}}}{I^2/\frac{\Delta R}{R}} = \frac{3.8 \times 10^{-6}}{0.921} = 345 \times 10^{-6} \quad (11)$$

Resistance changes from various applied currents were then measured for JP-4 and MEF-2, and the resulting curves are also shown in Figure 4. Thermal conductivity was calculated from the value of C and the slope of the lines as follows:

$$K_{\text{JP-4}} = C \times \frac{1}{\text{slope}} = 345 \times 10^{-6} \times 0.758 = 262 \times 10^{-6} \text{ cal/sec cm } ^\circ\text{C} \quad (12)$$

$$K_{\text{MEF-2}} = 345 \times 10^{-6} \times 0.700 = 242 \times 10^{-6} \text{ cal/sec cm } ^\circ\text{C} \quad (13)$$

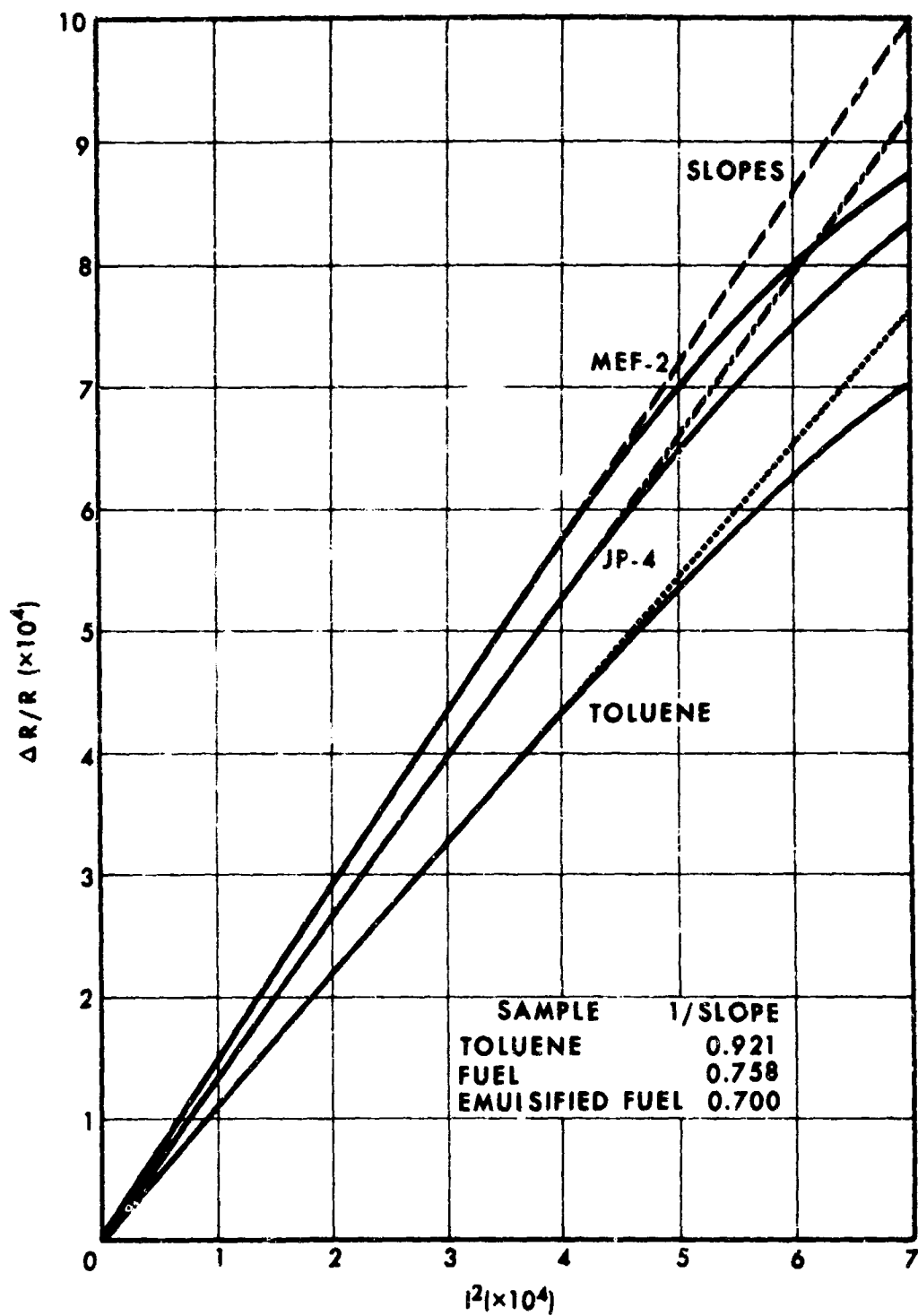


Figure 4. Wire Resistance Change vs Applied Current.

The accuracy of these determinations is difficult to determine because of the extreme variance of quoted K values and many other problems associated with measurement of liquid thermal conductivity. However, a rough estimate would place the figure at 10%. In this case, it appears that there is no significant difference between the thermal conductivities of JP-4 and MEF-2.

A detailed description of the apparatus and procedure used is listed in Appendix IV of this report. Also shown is a table of results, along with a photograph of the test equipment.

19. Heat Transfer Properties

In order to obtain some idea of the relative heat transfer coefficients of JP-4 and MEF-2, apparatus was set up whereby JP-4 and MEF-2 could be pumped at identical flow rates through a tube containing a controllable heat source. The preheater section of a standard CFR Fuel Coker was used for this test. It consists of two concentric steel tubes (1/2 inch and 9/16 inch in diameter, respectively) and a cartridge-type heating element which fits inside the inner tube. The length of the heated section is 12.5 inches. The fuel is pumped through the annular space between the two tubes by a variable-speed gear pump. The heater input is monitored by a wattmeter, and two in-stream mounted thermocouples measure the fuel temperature at the tube inlet and outlet.

In an apparatus as described above, the difference between the fluid outlet and inlet temperatures at identical heat input conditions is a measure, albeit a crude one, of the overall heat transfer coefficient of the apparatus. The larger this difference, the higher the mean value of the overall temperature difference between the heated surface and the bulk fluid; consequently, the lower the overall heat transfer coefficient. From

$$U = \frac{Q}{A \cdot \Delta T} \quad (14)$$

where U = overall heat transfer coefficient

A = heat transfer surface area

Q = heat transferred to the fluid

ΔT = mean value of the overall temperature
difference between the heated surface
and the bulk fluid

it is evident that indeed a larger ΔT results in a lower value of the overall heat transfer coefficient U. As explained above, this ΔT is not the difference between the fluid outlet

and inlet temperature, but can be related to it if all the descriptive parameters for the heat transfer process are known. For example, to establish such a relationship for our apparatus would necessitate data on the temperature distribution of the heated surface in contact with the fluid.

19.1 Test Procedure

It was observed initially that the emulsion flowed at a rate 20% slower than the JP-4 at the same pump speed setting. Therefore, higher speed settings for MEF-2 had to be experimentally utilized in order to obtain the flow rates of JP-4. JP-4 was first pumped through the annulus at pump speed settings near the top, middle, and bottom of the available range. Flow rates at these settings were volumetrically measured, and the density of JP-4 was determined so that the flow rates could be expressed on a weight basis. The heater was then turned on and a wattage setting was experimentally chosen whereby the temperature of the JP-4 would rise to between 120°F and 140°F at equilibrium flow conditions. This temperature range was chosen because emulsion breakdown could occur at higher temperatures. The JP-4 was allowed to flow 10 minutes at the heater wattage setting; after this time, an equilibrium temperature had been reached.

The MEF-2 (6 weeks old) was then pumped at the same flow rates and wattage settings, and its density was also measured. After 10 minutes with the heater on, the equilibrium temperatures were noted.

19.2 Test Data

Table XXX shows the data obtained in the above tests.

In evaluating these data, the accuracies of the following measurements must be taken into account:

1. The flow rate: ± 0.1 ml/min. for JP-4, but it may have been ± 0.5 - 0.8 ml/min. for MEF-2.
2. The temperatures: $\pm 0.5^\circ\text{F}^*$ for the fluid inlet and outlet temperatures.

*This does not take into account the radial temperature gradient in the annulus. It is estimated that laminar flow prevailed in all experiments; thus a radial temperature gradient does exist.

TABLE XXX. HEAT TRANSFER DATA						
Fluid	Flow Rate (ml/min)	Heater (watts)	Specific Heat (Btu/lb-°F)	Density @ 78°F (g/ml)	Inlet Temp (°F)	Outlet Temp (°F) ΔT (°F)
JP-4	52.6	80	0.500	0.757	78	138 60
MEF-2	52.6	80	0.511 ^a	0.734 ^b	82	146 64
JP-4	89.3	100			78	134; 136 ^c 57
MEF-2	89.3	100			82	142 60
JP-4	126.0	130			82	127 45
MEF-2	126.0	130			82	141 59
^a Calculated from the specific heat values of the major constituents: JP-4 (0.500), ethylene glycol (0.580), H ₂ O (1.00). ^b Theoretical density is 0.762 g/ml. The measured value of 0.734 g/ml can be explained by air entrainment in the MEF-2. 4% of air by volume will yield a density value as measured. ^c Two runs were made, and the average of the measured outlet temperatures was used to determine ΔT.						

The primary consequence of these errors is that at the lower flow rates (52.6 and 89.3 ml/min.), no meaningful conclusion can be drawn from the measured temperature differences for JP-4 and MEF-2. On the basis of the experimental evidence, the strongest statement that can be made is that the temperature differences observed for JP-4 and MEF-2 appear to be comparable and that the heat transfer properties of the two fluids are thus comparable under the conditions determined in the equipment and at the flow rates and heater inputs stated. The larger difference in ΔT between JP-4 and MEF-2 at the highest flow rate may be an indication either that the two fluids have different heat transfer properties or that the JP-4 data point is in error. For example, a good heat transfer fluid such as water would show a ΔT of only 30°F under the lowest flow rate condition in the table. This temperature difference was calculated using a formula described by Brown.²

19.3 Discussion of Results

The above results do not allow accurate conclusions to be drawn with respect to differences in thermal behavior of JP-4 and MEF-2. Based upon the two lowest flow rates, differences appear to be small and well within the error of measurement. However, this tentative conclusion is valid only for conditions prevailing in the test apparatus. An accurate evaluation of the test results is not possible without a detailed knowledge of the physical properties of the emulsion (such as its thermal conductivity, specific heat, viscosity, and density) over an appropriate range of temperature and flow conditions.

Heat transfer equipment utilizing MEF-2 cannot be designed without formulae (correlations) which relate the heat transfer coefficient to the thermophysical data, the flow conditions, and the heat transfer configuration. On completion of a thermophysical property measurement program, an experimental program to determine these relationships could begin.

20. Surface Free-Energy of Emulsion

The surface tension of MEF-2 emulsion was measured by the Wilhelmy method.³ This method involves measuring directly the pull of the surface of a liquid on the perimeter of a partially immersed body, such as a vertically hung platinum slide.

In practice, the slide is suspended from the left arm of a double pan Chainomatic balance and weighed. The position of the bottom edge of the slide is noted with a Cathetometer, and the slide is moved higher by the addition of more weight. A

petri dish containing the test fluid or emulsion is then raised by a lab jack so that the bottom meniscus of the liquid (or emulsion surface) is in the same plane as was the slide bottom when weighed. By removing weight, the slide is immersed in the liquid or emulsion; then weight is added to bring the slide back to its "weighed" position (via Cathetometer). The total weight required to do this is recorded as (G) in the following formula for surface tension:

$$\gamma = \frac{g(G - W)}{2(t + w)} \quad (14)$$

where $g = 980.7 \text{ cm/sec}^2$
 $W = \text{dry slide weight}$
 $t = \text{slide thickness}$
 $w = \text{slide width}$

Equilibrium is rapidly reached with liquids. With the emulsions, however, it was necessary to find that weight whereby the slide would quickly break through the surface, and then continually repeat the experiment with lesser weights (0.001-g increments) until a point was reached where the emulsion "held" the plate for at least 20 seconds.

The yield stress was measured on freshly prepared MEF-2 emulsion, and the surface tension was measured. The emulsion was then placed in two 1-gallon jars, which were then stored at 77°F for either 30- or 60-day periods. The yield stress and surface tension were again determined on the emulsion which had been stored for 30 days. The jar of emulsion was then shaken vigorously for two 5-minute intervals, and the yield stress and surface tension were determined after each interval. The results are shown in Table XXXI, along with experimental and "literature" values for several control fluids.

The differences in surface tension values for the emulsions are not considered to be experimentally significant. It thus appears that there is no significant correlation between yield stress and surface tension.

21. MEF-2 Metal Corrosion

Metal strips, 1 x 3 inches, were scrubbed in aqueous detergent solution with a nylon surgical brush and then rinsed successively in water, petroleum ether, and acetone. The weighed strips were then either half-immersed in a test fluid or tied together with another metal and completely immersed.

TABLE XXXI. SURFACE FREE-ENERGY OF MEF-2 EMULSION (Wilhelmy Plate Method)					
Fluid	Emulsion Age	Condition	Yield Stress (dynes/cm ²)	Surface Tension (dynes/cm)	Literature Value (dynes/cm)
Water		Platinum slide	-	72.3	72.6
Benzene		"	-	29.2	28.9
CCl ₄		"	-	27.2	28.0
Emulsion	1 hour	Freshly prepared	1200	23.6	
	30 days	77°F storage	680	24.7	
	"	Container shaken 5 min.	730	24.7	
	"	Shaken for another 5 min.	770	23.6	
	60 days	Different sample, 77°F	660	23.6	
	"	Container shaken 5 min.	740	24.8	
	"	Shaken for another 5 min.	780	23.6	
Differences in the surface tension values are not considered to be experimentally significant. Therefore, the surface tension remains essentially constant during storage at 77°F and is not affected by an increase or decrease in yield stress.					

Separate tests were run for both the MEF-2 emulsion (1% excess acid and 1 month old) and the JP-4 control for both single panels and couples. Tests were run at both 77°F and 140°F.

The test jars were stored 1 week at the above temperatures, and the metal strips were then cleaned and reweighed. The only variance from the initial cleaning procedure was that this time the coupons were brushed in water only.

The weight losses of all the metals in JP-4 were very small, and they were subtracted from the corresponding weight loss in MEF-2 to give a net loss due strictly to the emulsion. Inches per year corrosion penetration was then calculated from the equation

$$C = \frac{527 W}{ATS} \quad (15)$$

where C = inches/year

W = weight loss (grams)

A = exposed surface area (square inches)

T = time of exposure (hours)

S = density (grams/cc)

The results are shown in Table XXXII.

Most of the corrosion on single panels at both temperatures occurred below the surface of the emulsion. The metals generally corroded more when in the couples, although none of the corrosion was severe. The corrosion caused by MEF-2 was much less than that caused by MEF-1.

The metals that corroded most noticeably were magnesium, brass, and 4340 steel (transverse cut and heat treated to 280 ksi). The corrosion that occurred in the 7075 and 2024 aluminum alloys is no doubt due to the alloyed magnesium and copper.

No corrosion was observed on either the cold-rolled mild steel or the 304 stainless steel.

The corrosion figures for MEF-2 are in general markedly lower than those for MEF; of particular note is the absence of corrosion to mild or stainless steel. Corrosion of cuprous alloys was also at a much lower level than that for MEF. A light, white, powdery coating occurred with aluminum alloys, but weight gains or losses were negligible. It is apparent from these data that the MEF-2 formulation produces little corrosion either as single metal or as metal couples.

TABLE XXII. QUANTITATIVE CORROSION TESTS IN MEP-2 EMULSION ^a 7 Days, 77°F & 140°F; Half Immersion for Single Specimens, Total Immersion for Couples										
Test Metal	Number	Test Temp. (°F)	Single Specimen Tests			Other Metal in Couple	Tested With Metal Couple			Visual Appearance of Submerged Part of Test Metal
			Avg. Wt. Loss (mg)	MEP-2	Inches/Year ^b Penetration (Beyond JP-4)		Avg. Wt. Loss (mg)	MEP-2	Inches/Year ^b Penetration (Beyond JP-4)	
Aluminum	7075	77	0.4	0.4	0.0000	Brass	0.3	0.8	0.0001	Light stain
"	"	140	0.4	2.3	0.0007	"	0.6	1.9	0.0004	Shiny surface
"	2024	77	0.2	0.5	0.0001	4340	0.0	1.0	0.0003	Light stain
"	"	140	0.2	1.8	0.0006	"	0.1	2.8	0.0008	Shiny surface
Steel	Mild, cold roll	77	0.0	0.0	0.0000					No change
"	"	140	0.2	0.4	0.0000					No change
"	4340	77	0.2	0.3	0.0000	2024 Al	0.3	1.7	0.0001	Black interface spots
"	"	77				Magnesium	0.5	0.6	0.0000	No change
"	"	140	0.1	8.4	0.0008	2024 Al	0.4	4.9	0.0004	Interface spots, black stain
"	304 Stainless	77	1.5	1.3	--	Brass	-0.6	2.2	0.0001	No change
"	"	140	-0.1 ^c	-1.0	--					No change
Magnesium	Type III	77	0.5	0.6	0.0001	4340	0.0	2.7	0.0016	White stain
"	"	140	0.1	0.8	0.0004					Blackish stain
Brass	Type I, QQ-B-61B	77	0.0	3.5	0.0004	7075 Al	1.1	8.4	0.0007	Purple, blue, green spectrum
"	"	77				304 Stainless	1.1	7.7	0.0007	Purple, blue, green spectrum
"	"	140	-0.3	6.7	0.0008	7075 Al	0.2	11.6	0.0013	Purple, blue, green spectrum, but more reddish

^a MEP-2 emulsion was 1 month old and contained 1% excess acid.

^b Calculated from submerged surface area, metal density, test time, and weight loss.

^c Minus sign shows gain in weight.

NOTE: Above results are averages from duplicate tests.

^a MEP-2 emulsion was 1 month old and contained 1% excess acid.

^b Calculated from submerged surface area, metal density, test time, and weight loss.

^c Minus sign shows gain in weight.

NOTE: Above results are averages from duplicate tests.

22. Compatibility With Elastomers

The O-rings were the following:

MIL-P-5315 - Buna N
MIL-R-25897 - Viton Class I
MIL-R-25988 - Fluorosilicone

Volume change was determined in accordance with ASTM D 471-63T on triplicate O-rings immersed in JP-4 and MEF-2. Hardness change is the difference in hardness readings (Shore A, taken in accordance with ASTM D 676-59T) before and after immersion.

Tensile strength and ultimate elongation were determined in accordance with ASTM D 1414-56T on unexposed and immersed O-rings. The immersed rings were tested after evaporation of the test liquid.

The elastomer O-rings were exposed to JP-4 and MEF-2 for 70 hours at 77°F, with the results shown in Table XXXIII. Buna N was again most affected by the emulsion, as it was by the MEF emulsion. It was noticed that the MEF-2 emulsion surrounding the submerged Buna N O-rings began breaking down within several hours. Little or no emulsion breakdown occurred with the other elastomers, and their test values approximated those in JP-4.

23. Vapor Loss

Vapor loss as a function of time was determined for the MEF-1 and MEF-2 emulsions at 77°F and 140°F. A petri dish 3-13/16 inches in diameter and 1/2 inch deep was filled with emulsion and leveled with a straightedge. The dish was weighed empty, full, and again every hour as it sat either in ambient air or on a hotplate. The same petri dish was used for all emulsions at the particular temperature.

The emulsions at 77°F were set on a marked spot in a vented hood, while the emulsions at 140°F were set on a marked spot of a hotplate in the same hood. The hotplate temperature was controlled with a Variac. The voltage setting was predetermined by adjusting until emulsion in the petri dish reached and maintained 140°F. Each emulsion or fuel was run at this setting while a smaller dish of emulsion containing a thermometer continually monitored the temperature consistency at the edge of the hotplate. The results at 77°F are shown in Figure 5, while these at 140°F are shown in Figure 6.

After 1 hour at 77°F, the MEF-1 emulsion lost only one-eighth as much weight as JP-4; the MEF-2 emulsion lost only one-seventh as much weight as JP-4. After 1 hour at 140°F, the

TABLE XXXIII. ELASTOMER COMPATIBILITY - O-RING RESISTANCE TO JP-4 AND MEF-2 70-Hour Exposure @ 77°F													
Type O-Ring	Immersion Medium	Tensile Strength (psi)				100%		% Elongation		% Volume Change		Hardness Change	
		Failure		Elongation		Rep	Avg	Rep	Avg	Rep	Avg	Rep	Avg
		Rep	Avg	Rep	Avg								
Buna N	None	1480		452		218		218					
		1450	1520	452	450	218	218						
		1630		452		216							
	JP-4	1550		516		225		210		11.0		0	
		1520	1400	484	505	218	210			9.5	10.3	+1	0
		1150		516		180				10.3		-1	
Viton I	None	1230		484		188		200		16.5		-1	
		1230	1270	484	480	194	200			16.5	16.4	0	-1
		1370		468		213				16.3		-1	
	JP-4	1740		484		257		235					
		1230	1600	516	515	193	235						
		1820		548		257							
Fluoro-silicone	None	1580		565		218		255		3.5		0	
		1770	1700	484	500	264	255			3.6	3.9	+1	0
		1740		452		276				4.6		0	
	JP-4	1500		548		218		230		4.1		0	
		1790	1560	581	560	251	230			4.2	4.5	+2	+1
		1400		548		218				5.1		0	
MEF-2	None	672		534		119		110					
		552	605	517	525	106	110						
		586		517		112							
	JP-4	548		500		109		105		11.9		-2	
		452	515	-	500	95.8	105			12.2	12.0	-2	-2
		548		500		109				12.0		-2	
MEF-2	JP-4	232		-		64		100		14.1		-3	
		606	495	497	490	115	100			12.9	13.8	-1	-2
		645		484		128				14.3		-1	

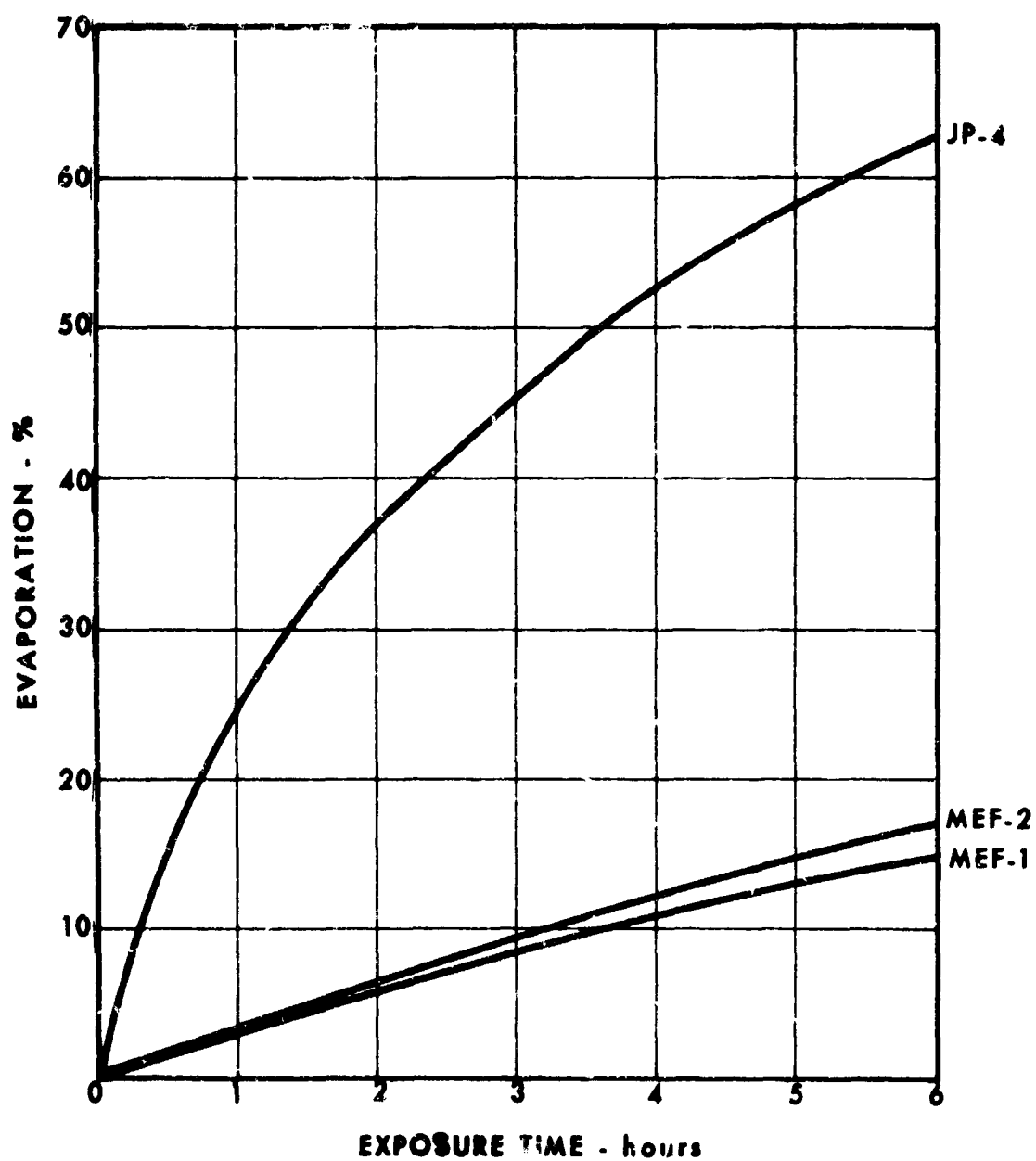


Figure 5. 77°F Evaporation Rate of MEF-1 and MEF-2 JP-4 Fuel Emulsions.

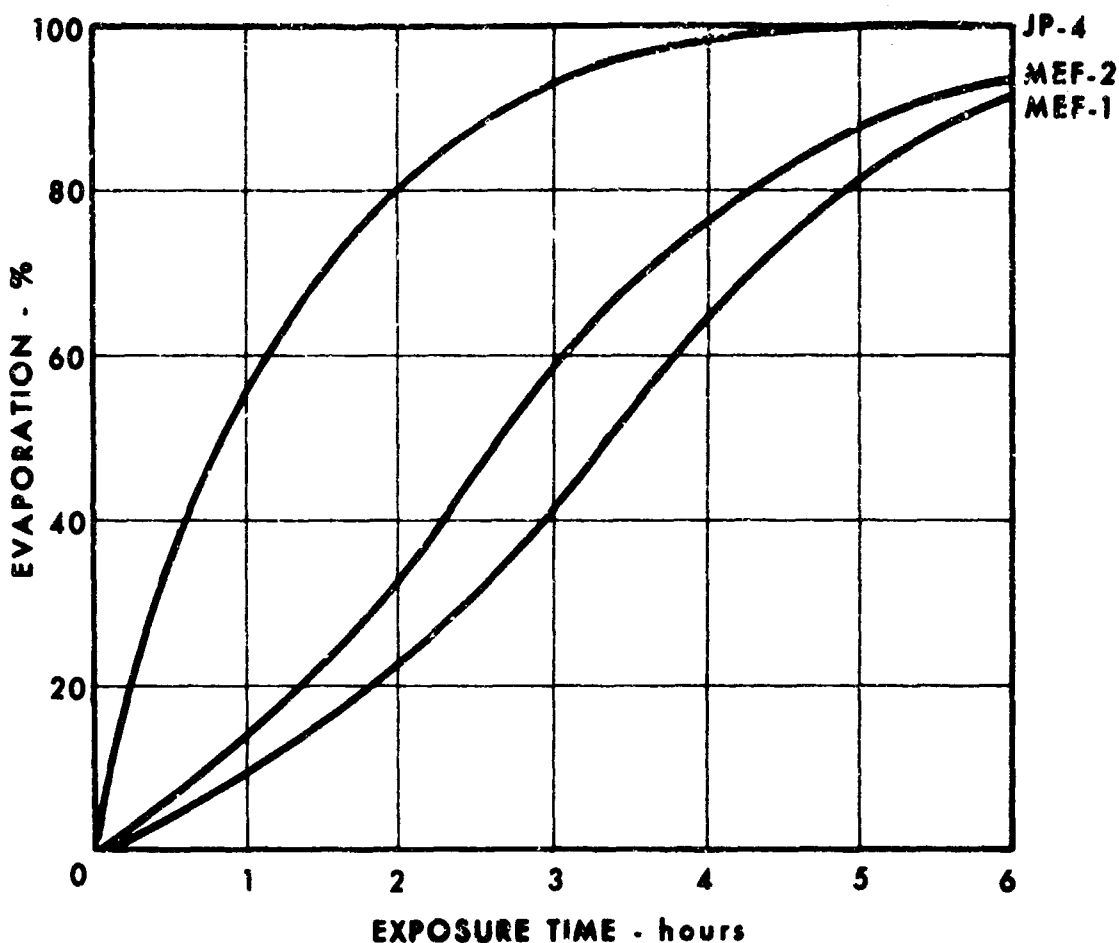


Figure 6. 140°F Evaporation Rate of MEF-1 and MEF-2 JP-4 Fuel Emulsions.

MEF-1 emulsion had lost about one-sixth the weight that JP-4 lost, while the MEF-2 emulsion had lost about one-fourth the weight. The MEF-2 emulsion had completely broken after 3 hours at 140°F, while the MEF-1 emulsion required 4 hours for complete breakdown.

24. Microbial Resistance

The susceptibility of emulsified fuel to microbial growth was determined during the previous contract, using the following predominantly fuel-utilizing organisms: bacteria in the genus *Pseudomonas* and fungi in the genus *Hormodendrum* (*Cladosporium*).

The two emulsions tested were based upon the tallow amine acetate MEF formulation, one sample containing a biocide and the other not. No difference between the two formulations was apparent, nor did they differ from the free JP-4 in support of bacterial growth. Under some conditions, growth of a *Hormodendrum* sp. was decreased when emulsified fuel served as the carbon growth source.

Using the same conditions and organisms, MEF-2 provided essentially the identical results obtained with MEF emulsions. As in the first study, no difference from JP-4 was found in the bacterial cultures.

The details of this test program, carried out under subcontract by the Department of Biology of the University of Dayton, are given in Appendix V.

25. Emulsion Preparation

The emulsion can be made in two ways: (1) by direct formulation, reacting the acid and amine in the required amount of ethylene glycol and adding water, followed by emulsification of the fuel; or (2) by preparation of an external phase concentrate of emulsifier in the glycol, transferring this in the required amount to the mixer, adding water, then emulsifying the fuel.

Quality conformance tests must be made on both the glycolic acid and the amine using the methods cited in Section 9. Since the emulsifier is based on a given quantity of the amine and stoichiometric quantity plus 1% for the glycolic acid, calculations for each must be made, and a further correction for deviation of the acid content from the "apparent" commercial 70% is necessary. The following steps are taken:

- A - Determine concentration of commercial glycolic acid, e.g., 70%.
- B - Glycolic acid used in emulsifier for stoichiometry, e.g., 22.08% based on Foremost amine.
- C - Glycolic acid used in B + 1% excess, e.g.,
B + 0.01B, 22.30%.

25.1 Direct Emulsion Formulation

	100% Basis	Acid Used	
		(A) Commercial	70% Commercial
Wt % EG	1.310	1.310	1.310
Wt % Acid	0.111	0.111/A	0.159
Wt % Oleyl Amine	0.389	0.389	0.389
Wt % Water	2.190	$2.19 - (\frac{0.111}{A} - 0.111)$	2.142
Wt % JP-4	96.00	96.00	96.00

25.2 Emulsion Formulation From XPC

	100% Basis	Acid Used	
		(A) Commercial	70% Commercial
Parts EG	72.38	72.38	72.38
Parts Acid	6.13	6.13/A	8.67
Parts Oleyl Amine	21.49	21.49	21.49

25.3 Emulsion

	100% Basis	Acid Used	
		(A) Commercial	70% Commercial
Wt % XPC	1.81	$1.699 + \frac{0.111}{A}$	1.858
Wt % Water	2.19	$2.19 - (\frac{0.111}{A} - 0.111)$	2.142
Wt % JP-4	96.00	96.00	96.00

PHASE II. DEMULSIFICATION

1. General

The contract called for a continuous process for emulsion breakdown and JP-4 separation. This process was to be demonstrated on a small-scale basis (2-3 gallons per minute) and be capable of being scaled to 500 gpm. Both shear and chemical means of demulsification were to be investigated.

Shear recovery is desirable for its potential simplicity and because no purification of the recovered fuel may be necessary (see the discussion on JP-4 quality). In its simplest form, a shear recovery system might comprise two items: the shear device and either a liquid cyclone or a centrifuge.

Rather than attempt to develop a new shear device, it was decided to look for a commercially available piece of equipment that would be applicable to this problem. Therefore, representatives were interviewed from various companies selling pumps, mixers, blenders, colloid mills, and homogenizers and exhibiting at the Exposition of Chemical Industries. Some of the possibilities and conclusions resulting from these discussions were as follows:

- Centrifugal pumps will neither handle the emulsion completely successfully nor provide enough shear to completely break it.
- A shear pump is available which is a combination pump and shear device. However, its limiting factor is a maximum through-put of 30 gpm.
- Certain rotary pumps impart more shear than centrifugal pumps, and these were to be investigated. They also have the advantage of being positive displacement pumps and should transfer the emulsion without difficulty. A drawback to any pump in breaking emulsion is the short "dwell time" of the emulsion in the pump.
- If longer dwell times are required, a pump in series with a high-speed mixer or blender should produce satisfactory shear and fluid transfer.
- Homogenizers and some colloid mills impart more shear than a blade blender, but they are bulky pieces of equipment, overengineered for our purpose. These also have a top operating capacity of only 200 gpm.

- The sonic device is said to be one of the highest-intensity mixing devices available. A flat, high-pressure jet stream of fluid impinges on the edge of a flat blade and causes intense ultrasonic vibration within the liquid itself. The resulting cavitation causes violent local pressure changes which are converted to high-intensity mixing energy. These models can be scaled to handle 500 gpm.

These preliminary discussions with the manufacturers were used to provide background and to determine whether the equipment people would perform preliminary trials with their equipment to minimize our total effort.

The principles of operation of the various types of equipment discussed and evaluated were:

- Counterrotating discs with dispersion bars
- In-line turbine
- In-line turbine and stator
- Rotor/stator combination
- Rotor/stator, 3 sets of mating surfaces
- High-velocity stream through restricted orifices
- Membrane filters and coalescer
- High-pressure jet stream impinging on vibrating head

2. Preliminary Laboratory Experiments With Shear Equipment

Experiments were made with available laboratory equipment to attempt to estimate the magnitude of shear required to break the emulsion.

2.1 Blade Blender

The blade blender is widely used in laboratory work because of the shear attained by the high-speed (19,000 rpm), four-bladed rotor. Depolymerization of ordinarily stable polymers can be attained with this equipment.

A 19,000-rpm blender broke only about half of 100 ml of MEP-2 after 5 minutes. Most of the emulsion that broke did so during the first several seconds. Apparently the rest of the emulsion, being denser than JP-4, was flung away from the rotating blades against the container walls.

2.2 Centrifugal Pump

A 3400-rpm centrifugal pump broke part of the emulsion after multipasses, but it broke none during a single pass. The

resulting JP-4 after shear breakdown was cloudy and had to be centrifuged. However, the freed emulsifier remained in the amine acetate form, and most of it dissolved in the water phase rather than the JP-4. This was also the case with the MEF-2 emulsion.

2.3 Internal Rotary Gear Pump

A small (3 gpm) rotary gear pump mounted directly to a 1/4-horsepower motor was rented from a local distributor. It is a positive-displacement pump which imparts more shear than a standard external gear pump. For the first run, a piece of 1/2-inch copper tubing was bent into a "U" shape, and one end was fastened to the pump inlet. The other end was submerged in a container of emulsion mounted above the pump. When the pump was started, a flow of only about 0.5 gpm was obtained. When the copper tube U-bend was eliminated and a container was mounted directly above the pump inlet, so that emulsion could flow out the bottom through a short piece of tubing, the flow rate increased to about 2.5 gpm. Thus, the bends in the copper tubing must have acted as restrictions in the first trial. With 1 inch or longer tubing, the bends probably would not have been significant. The need for pump priming is significant.

The MEF-2 emulsion was passed through this pump with the hope that the emulsion would break. However, no breakdown was detected.

2.4 High Shear Mixer - Open System

This mixer incorporates a rapidly spinning toothed disc at the end of a shaft. The teeth are perpendicular to the disc, above and below, and are designed to generate high shear as well as rapid circulation in viscous fluids.

It was found that this mixer with a 3-1/2-inch-diameter disc would break about 50% of the MEF-2 emulsion in a container 4-1/2 inches in diameter after only several seconds of agitation. As soon as the emulsion began to break, the liquid JP-4 was thrown out of the container and the mixer had to be shut down.

A closed system was built out of pipe to fit around the mixer blade so that this mixer could be evaluated better. The emulsion was pumped into the bottom of the tube assembly, past the perpendicularly rotating disc, sheared against baffles, and ejected from an overflow pipe for evaluation.

2.5 High Shear Mixer - Closed System

A closed system made of 2-1/2-inch pipe connections was built around the 1-3/4-inch blade of the mixer (12,000 rpm). The pipe was mounted vertically and the mixing blade rotated in a horizontal plane. Two 1-5/8-inch x 2-3/8-inch washers were welded inside the pipe an inch above and below the blade to act as baffles and to direct the emulsion flow toward the blade.

The emulsion was pumped into the bottom of the assembly by a 3-gpm gear pump, gravity fed through a mounted funnel. The pump and mixer were turned on simultaneously, and a container was placed at the outlet. Unexpectedly, the emulsion emerged completely unbroken. Apparently, the emulsion was compressible enough to flow around the blade without being highly sheared. Even when the pump was stopped, the residual emulsion in the tube remained unbroken by the action of the mixer.

These results combined with those of the blender test indicated little hope for breaking the emulsion with an in-line mixer.

3. Investigations by Equipment Manufacturers

The principles of operation of the several types of equipment potentially applicable to mechanical demulsification have been previously explained. The objective of these tests was to have the manufacturer examine the emulsion in his equipment under his best conditions of operation to determine potentiality. Any process that was 50% or more effective then became a candidate for further evaluation under Monsanto Research Corporation supervision.

The counterrotating disc with dispersion bars successfully broke the MEF-2 emulsion, with about 90% breakdown at 1000 rpm and about 97% breakdown at 1500 rpm. However, this mixer has a top capacity of only 110 gpm.

The in-line turbine with stator failed to break the emulsion.

Rotor/stator colloid mills tested for demulsification using several different pieces of equipment were unsuccessful in breaking the MEF-2 product. The rotor/stator mill with three sets of mating surfaces also failed to break the emulsion.

One principle which appeared to yield greatest demulsification was that operating in effect as a spray device. The emulsion under high pressure was ejected through small apertures, the pressure drop and shear at the orifice resulting in 90-95% MEF-2 demulsification.

4. Laboratory Investigations of Potentially Useful Equipment

This section describes the testing of three of the potentially more effective and applicable systems for demulsification.

4.1 Rotor/Stator Colloid Mill

A rotor/stator colloid mill and a variable-speed pump were loaned for MEP-2 breakdown trials. However, 10% breakdown was the maximum that could be obtained with the equipment.

The variable-speed gear pump had a maximum capacity of 3.5 gpm, while the colloid mill could produce 1.6 gpm. In the trials, the gear pump was varied from one-third to full speed, while the rotor-stator gap was varied from 0.002 to 0.026 inch. Both the rotor and stator were grooved for maximum shear.

When the partially broken emulsion was recycled through the colloid mill, no additional emulsion was broken. In fact, the unbroken part of the emulsion was observed to be thicker after the process.

4.2 Membrane Filter and Coalescer

The liquid separator is a combination of a coalescer cell and two preferentially conditioned tubular membranes. It is used mainly in the process industries to separate stubborn, unstable emulsions. For our problem, it was hoped that pumping the emulsion through the coalescer cell would cause breakdown; then the two phases could be separated by the tubular membranes.

The membrane filters are uniform, porous, metal structures available in porosity grades ranging from a 5-micron diameter down to a 0.2-micron diameter.

The liquid shearing operation was accomplished by passing the emulsion via vacuum through 5-micron and 0.8-micron metal membranes in series. The 5-micron membrane prepared the emulsion for passage through the 0.8-micron membrane, and the 0.8-micron membrane was necessary for maximum effective separation. Membranes finer than 0.8 micron could be utilized, but premature plugging occurred. The reason was not apparent, but it was suspected that small rust particles contained in the JP-4 used to make the emulsion might have been responsible for the plugging.

The proposed system consists basically of liquid shearing through the two metal membranes mentioned above, a holding tank where most of the fuel floc would settle and be drawn

off, followed by a coalescer where the JP-4 would be completely clarified. Presumably, pressure pumps operating at as low as 15 psi can accomplish the job. This system is said to be capable of being scaled to 500 gpm.

All the evaluation was done by the equipment manufacturer, and actual trial under Monsanto Research Corporation direction was not accomplished.

4.3 High-Pressure Jet Stream and Vibrating Reed

Preliminary tests by the company manufacturing this equipment indicated that it broke about 85% of the MEF-2 emulsion using a high-pressure jet stream equipped with a 0.042-inch orifice. The instrument operated at 8 gpm and 500 psi.

The broken emulsion separated immediately (several seconds) into 50% clear JP-4 and 50% loose gelled floc. The loose floc passed readily through a coarse filter to obtain a total of 80% clear fuel.

An analysis of the recovered JP-4 showed only 1.5% of the oleyl amine present, amounting to a total concentration of 0.006%.

It appeared that very little centrifugal force would be necessary to remove the gel floc and that a liquid cyclone (centrifuge operated by pressure) should be sufficient to accomplish the task.

Two versions of this device were tested at Monsanto Research Corporation: one a low-pressure device, and the second for high-pressure usage.

The low-pressure unit consisted of a 10-horsepower motor, a 10-gpm gear pump, and the high-pressure jet stream, in series. The emulsion was pumped through a small orifice and then across a vibrating blade. The pressure drop and vibrational energy then combined to break the emulsion.

The machine manufacturer had been able to break 80% of the emulsion at 500 psi produced by a continuous-cavity pump. It was hoped that higher pressures (perhaps 1000 psi) obtained with a gear pump would produce a greater degree of emulsion breakdown. However, initial runs with supplied orifices produced only 400 psi and about 80% breakdown.

Orifices with slit widths of 0.042, 0.034, 0.025, and 0.017 inch were tried. The upstream pressures obtained with these orifices were 380, 440, 500, and 600 psi, respectively. Little

or no cavitation energy was obtained with any of the orifices, and the amount of MEF-2 breakdown varied from 60-80% by volume, with the greater breakdown occurring at the highest pressure.

When the vibrating reed was adjusted to the position closest to the orifice, the operating pressure increased from 600 psi to about 1000 psi with the 0.017-inch orifice. No cavitation energy was registered; however, the amount of emulsion breakdown increased to nearly 90% at this pressure.

Because the 1000-psi pressure was obtained under unnatural conditions and because of the unexplained lack of cavitation energy, the device was returned to the company. In its place, Monsanto Research Corporation received a high-pressure device identical except for a gear pump of variable speed. Whereas the pump on the previous machine was operated at 520 rpm, the new pump had an operating range of 300-950 rpm. It was felt that this would be more than enough to obtain 1000-psi readings.

Very strong energy signals were obtained with all orifices; however, a maximum operating pressure of only 450 psi was obtained with the 0.017-inch orifice. Moving the vibrating reed nearest the orifice increased the operating pressure to only 600 psi and lowered the cavitation energy to almost zero. In both cases the amount of emulsion breakdown was less than 80%.

The variation in results obtained with the two devices showed the importance of high-pressure drop for optimum emulsion breakdown. Apparently, nearly 1000 psi is needed for satisfactory results. Also of interest is the fact that the emulsion pumps at a lower pressure than JP-4 at identical pump rpm.

Because of the time required to ship and install another version of the machine, other trials were run at the device manufacturer's laboratory. Fifteen gallons of emulsion was sent for trial in the high-pressure device operated by a variable-speed, six-stage continuous-cavity pump. This pump is known to operate at 1000 psi with water, and hopefully this pressure could be obtained with emulsion. Again, the recovery was not greater than 90%.

The device manufacturers believe that a high-speed centrifugal pump would work very well with this machine at flow rates near 500 gpm. These pumps are much smaller and more economical than comparable gear and continuous-cavity pumps.

5. Summary of Shear Tests

This investigation demonstrated that shear devices most effectively break the emulsion and operate on the principle either of pressure drop through a small orifice or of pressure drop through many very small orifices. In either case, it is necessary to separate the maximum 90 volumes of broken JP-4 from a floc consisting of 10 volumes of external phase. The JP-4/floc separation can be attained by centrifugation, by cyclone centrifugation, or by a coalescer system. Since a continuous operation from emulsion feed to JP-4 to the aircraft is desired, this would appear to eliminate a settling operation between the shear and coalescence stages.

With a maximum recovery of 90 volumes of JP-4, the residual 10 volumes comprises about 3.5 to 4 volumes of external phase and tightly emulsified JP-4. The residual floc represents a problem, either for recovery or for safe disposal. The only effective recovery system appears to be further demulsification by chemical means, but this presupposes a recovery and treatment system on the assumption that the oleyl amine in the JP-4 is engine combustible without potential hazard.

The ultrasonic reed device demonstrated that the laboratory size had a capacity to break emulsion at the rate of about 10 gpm, and the manufacturers indicate that the high-capacity unit can treat 500 gpm.

The membrane filter and coalescer device was indicated as handling up to 5 gpm on the laboratory basis, but whether a 500-gpm rate could be attained was not known.

6. Chemical Demulsification

While it is possible to break MEF emulsions rapidly with ammonia or ammonium hydroxide, two deficiencies exist in this system. The first is a matter of logistics in supply of aqueous ammonia, or a need for more extensive equipment with gaseous ammonia. The second is that essentially all of the oleyl amine is transferred to the fuel, a potential handicap in fuel combustion and/or deposit formation. Other, simpler means for accomplishing the objective of an essentially "clean" separated JP-4 were sought.

Emulsion breakdown by chemical means was previously demonstrated on MEF emulsion by the addition of 0.3% ammonium hydroxide. The breakdown was fast, and the resulting JP-4 was essentially clear. However, nearly all of the tallow

amine emulsifier released by the ammonium hydroxide dissolved in the recovered JP-4 and had to be removed by clay filtration.

The same situation occurs with the MEF-2 emulsion. The emulsion breakdown is perhaps slightly faster, since glycolic acid is stronger than acetic, and the freed oleyl amine then dissolves in the JP-4. Attempts were therefore made to chemically remove the oleyl amine from the recovered JP-4.

Sufficient ammonium hydroxide was added to break an MEF-2 emulsion. Immediately thereafter, an excess of acid was added to form an amine salt in the hope that this would become soluble in the water-EG phase. Both acetic and hydrochloric acids were tried, and each time the centrifuged JP-4 still contained all of the amine. Some buffering action was noticed in the trial with HCl.

Other attempts were made to rid the JP-4 of oleyl amine by chemical precipitation reactions. Acetic anhydride and benzoyl chloride were added to separate samples of the JP-4 in the hope of forming insoluble amides. However, none formed.

Various acidic chemicals were added to MEF-2 to break the emulsion. It was hoped that acids stronger than glycolic would preferentially react with the oleyl amine, break the emulsion, and then allow the freed glycolic acid to dissolve in the water phase. Sulfuric, hydrochloric, and phosphoric acids broke the emulsions at much slower rates than the hydroxide bases. Sulfuric acid caused the JP-4 to turn red; and when the other two acids were used, about 12% of the oleyl amine was still found in the recovered JP-4.

An acidic reactant (an acid phosphate ester with a pH of 2) contains 9-1/2 moles of ethylene oxide for water solubility. One-percent addition to MEF-2 with vigorous stirring broke the emulsion, and none of the amine dissolved in the JP-4. At higher than room temperature, the emulsion broke much faster. However, this surfactant is a thick gel-like liquid, and its injection into a continuous stream of MEF-2 for breakdown would be very difficult.

Another acid surfactant is dodecylbenzene sulfonic acid as 97% sulfonic acid. It is a thin liquid and broke the emulsion more readily than the other acids. However, the recovered JP-4 was found to contain strong acid.

The only completely successful method for rapidly breaking the emulsion chemically is still the ammonium hydroxide procedure.

7. Recovered JP-4 Quality

During the previous contract, it was shown that the chemical approach to JP-4 recovery from the emulsion was efficient when operated in two stages: separation followed by purification. As a result of the separation stage, the emulsion was broken quantitatively, the tallow amine remaining in the fuel. Should it be possible to burn this directly in the turbine without adverse effects, the process would be quite simple: breaking the emulsion in a continuous system, removing the external phase gravimetrically either by settling or by centrifuge, or passing the broken system through a coalescer system. However, if tallow amine proved to be deleterious, an adsorption column would be necessary.

Earlier sections of this report demonstrated that emulsion broken mechanically, i.e., by shear, resulted in negligible retention of emulsifier in the fuel, the bulk remaining in unbroken external phase. The best separation obtained was about 90%, a 10% external phase/fuel floc remaining unseparated under the best of conditions. However, the 90% product would further be cleaned by centrifugation or coalescence to remove unbroken external phase. Under the shear recovery system, since the perfectly clear fuel can be obtained, the main concern would be whether existent or potential gum level (probably as the dissolved emulsifier) was abnormally high. These tests were chosen as definitive since the MIL-T-5624G test methods are essentially artificial, though relatable to practice. Little further definable information would have been obtained through complete qualification testing.

Table XXXIV shows a comparison of the JP-4 used and that recovered by shear in the jet device at 1000 psi and 90% recovery. The recovered fuel was gravity settled to a perfectly clear state before it was sampled for test.

The data of Table XXXIV indicate that the gravity-settled recovered fuel was slightly higher both in existent gum and potential total residue than specification limits. Had the fuel been run through a coalescer, as in practice, it is very likely that finely suspended external phase would have been removed and the specification limits would have been met.

TABLE XXXIV. GUM IN SHEAR-RECOVERED FUEL			
	JP-4 As Used	Recovered JP-4	MIL-T-5624G Specification
Existent Gum, mg/100 ml ASTM D 381 (Steam Jet Method)	2.4 (2.0)*	8.4 (1.0)*	7 max.
Total Potential Residue, mg/100 ml ASTM D 873 (Accelerated Gum, 16 hr)			
Soluble gum	7.0 (2.2)*	20.6 (18.2)*	14 max.
Insoluble gum	0.0	0.0	
Precipitate	0.0	0.0	
Total potential residue	2.2	18.2	
*Solvent-washed gum residue			

SUMMARY OF RESULTS

PHASE I - MEF-1 DEVELOPMENT

Examination of emulsions prepared from a 168-formulation matrix showed that the preferred formulation had the following composition:

	<u>Wt. %</u>
External Phase	4.0
Tallow amine acetate emulsifier (2.2% excess acetic acid)	0.50
Ethylene glycol (37.5%)	1.31
Water (62.5%)	2.19
JP-4	96.0

The effect of excess acid upon stability showed that the pH should be about 4.8 and that an excess of acetic acid calculated at 2.2% greater than stoichiometric provided maximum stability.

Droplet size was median at 4 to 5 microns, with a range of 1 to 10. Method of emulsion preparation had a greater effect upon droplet size than variables of emulsion constitution.

Yield stress values were represented by the following:

At once - 1400 dynes/cm²
30 days at -16°F, measured at 0°F - 5800 dynes/cm²
30 days at 77°F - 730 dynes/cm²
30 days at 140°F - 400 dynes/cm²

Improvement in cold stability by using coupling agents was marginal, the most effective agents being isopropanol or tert-butanol, replacing 20% of the ethylene glycol.

Use of corrosion-preventive additives proved to be unsuccessful when over 20 typical chemicals of several types were added to the formulation.

A most significant improvement in corrosion prevention was obtained when either of two hydroxy acids, e.g., hydroxyacetic (glycolic) or lactic (hydroxypropionic), was substituted for acetic acid. No great difference was evident between the two,

but because of greater availability (and lower cost), glycolic acid was chosen for subsequent testing. An excess of glycolic amounting to 1% greater than stoichiometric was demonstrated as optimum for emulsion stability.

MEF-2 DEVELOPMENT

The improvement in formulation having been minor using the tallow amine acetate, the emulsifier was further examined, using the same type amine/acetate system but changing from the solid tallow amine to the fluid oleyl amine. Emulsions made with this surfactant exhibited excellent cold stability.

To verify the desirable properties of the oleyl glycolate emulsion, the optimum amount of emulsifier, the external phase, and the ratio of ethylene glycol to water were again determined. The optimum MEF-2 formula was:

	<u>Wt. %</u>
External Phase	4.0
Oleyl amine glycolate (1.0% excess acid)	0.50
Ethylene glycol (37.5%)	1.31
Water (62.5%)	2.19
JP-4	96.0

The following properties of the MEF-2 emulsion indicate its applicability.

1. Corrosion

Corrosion was negligible on mild steel; brass corrosion was reduced to one-third to one-half that of MEF-1.

2. Yield Stress

When tested at once, the yield stress in dynes/cm² was about 1300. After 1 day at 0°F, and tested at 0°F, the yield stress was about 1300. After 30 days at -30°F, and tested at 0°F, the yield stress was about 1000. After 30 days at 77°F, the yield stress was 750, while after 30 days at 140°F, a value of about 500 was obtained.

The emulsion was physically stable for extended periods at -65°F.

3. Specific Gravity

After 2 hours, a fresh emulsion had a specific gravity of 0.665 ± 0.001 with a yield stress of 1050 dynes/cm². After 10 weeks at 77°F, the emulsion had a specific gravity of 0.731 ± 0.001 with a yield stress of 780 dynes/cm². Increase in specific gravity is attributed to emulsification of air in the system, and at least part of the yield stress change is attributed to this same factor.

4. Emulsifier Solubility

Oleyl amine glycolate from the emulsion was soluble to the extent of 0.0015-0.0018% in the JP-4 recovered when the emulsion was broken by shear in a blade blender. The emulsifier remained essentially in the external phase.

5. Droplet Size Change With Age

Only slight change in droplet size occurred after 60 days at 77°F; this change was mainly in the top half of a 15-inch-high stored emulsion. The maximum change occurred in the top 2 inches, the range increasing from 1-7 μ to 3-10 μ .

6. Emulsifier Migration

At 500 g's for 5 days at the upper level of the emulsion, the amount of emulsifier dropped to 83.9% of that initially present, showing the considerable stability of the emulsion.

7. Agitation After Aging

A gear pump operated at 1800 rpm at 5 gpm in a single pass gave a yield stress of 660 dynes/cm². A centrifugal pump at 3500 rpm and 17 gpm for a single pass gave a yield stress of 780 dynes/cm². The 90-day-aged emulsion initially had a yield stress of 630 dynes/cm². Again, increase in yield stress can be attributed to air incorporation.

8. Thermal Conductivity

This value is an involved one, dependent upon density and viscosity among other parameters. However, the data from these tests indicated no significant differences between JP-4 and MEF-2, justification for this conclusion being based upon comparative values obtained with other fluids.

9. Heat Transfer Properties

Because of the equipment used and the need for thermophysical data, flow conditions, and heat transfer configuration, as well as experimental variation, accurate conclusions could not be drawn. However, for the two lower flow rates, differences between JP-4 and MEF-2 were small and within the allowable error of measurement.

10. Surface Free-Energy

The surface free-energy for the MEF-2 emulsion tested at once or after 60-day storage (77°F) measured 23.6 to 24.8 dynes/cm. Shaking prior to measurement had no effect upon surface tension, and a comparison of yield stress vs. surface tension gave a nearly constant value over the 60-day period. The surface tension of the emulsion approached that of JP-4.

11. Metal Corrosion

MEF-2 had practically no effect upon mild or stainless steel. A white, powdery deposit on aluminum alloys was apparent, but it resulted in negligible weight gain or loss. MEF caused much greater corrosion of magnesium, cuprous alloys, and 4340 steel than did MEF-2.

12. Compatibility With Elastomers

Of three elastomers tested, only Buna N showed any real effect of exposure, and there was less effect through MEF-2 exposure than through MEF.

13. Vapor Loss

Vapor losses for MEF and MEF-2 were essentially the same, and both were more resistant to loss than JP-4.

14. Microbial Resistance

Microbial growth of two hydrocarbon-growth organisms was essentially unaffected by MEF-2 and was equal to JP-4 alone in this respect. If anything, the fungus was adversely affected in the MEF-2 medium.

PHASE II - DEMULSIFICATION

The approach taken was that, of the many methods for applying shear to make or break emulsions, the most rapid and effective was by direct approach to manufacturers of such equipment. Nine producers were contacted after a preliminary screening at the Exposition of Chemical Industries.

1. Preliminary Experiments

Preliminary trials by centrifugal pump, blade blender, rotary gear pump, and high-shear toothed disc showed that up to 50% demulsification (blender) could be obtained.

2. Investigations by Equipment Manufacturers

Five firms having equipment believed to be effective for demulsification experimented in their own laboratories, and of these only three showed potential.

3. Investigation of Potential Equipment

A rotor/stator colloid mill provided only very partial demulsification.

A liquid shear-coalescer was claimed to give a 90% breakdown by passage through micron-sized membranes, but the manufacturer failed to qualify the apparatus for a continued run, even though the system was believed to be capable of 500 gpm.

A pressure drop-vibrating reed device was tested in two versions at low and high pressure. Either 500 or 1000 psi produced 80 to 90% demulsification (without the ultrasonic reed being effective) at a rate of 10 gpm. It was claimed that a high-capacity model will break 500 gpm.

None of these methods could completely resolve the emulsion, and the 10% residue represents a problem in disposal.

Chemical demulsification can quickly break the emulsions in entirety, but it represents a problem in logistics: the ammonium hydroxide and attapulgite clay are bulky, and the latter is needed in considerable volume. Other approaches at breaking the emulsion were unsuccessful. If oleyl amine were JP-4-compatible, the attapulgite adsorption would be unnecessary.

The quality of the JP-4 recovered from MEF-2 was estimated by determining existent gum and total potential residue. These were respectively 8.4 and 20.6 (mg/100 ml) for the recovered JP-4 vs. specification maxima of 7 and 14.

CONCLUSIONS

Phase I of the work statement, which concerned optimization of the MEF JP-4 emulsion, resulted in a greatly improved formulation. The optimized MEF-2 formula resulted in minimized corrosion characteristics, improved thermal stability, and sharp reduction in the effect of temperature on yield stress values.

As a result of Phase II investigation, it is concluded that though shear devices will partially break MEF-2, greater demulsification is obtained using either membrane filters and coalescer or jet pressure drop devices. In no case, however, were the devices capable of greater than 90% effectiveness. The 10% volume of unbroken emulsion, then, presents either a recovery or a disposal problem. An essentially quantitative demulsification can be obtained by chemical treatment (i.e., ammonium hydroxide addition) followed either by a coalescer or by centrifugal separation of the external phase. With this system the emulsifier amine remains in the fuel, whereas shear methods reduce the residual amine to 3% quantities of that originally present.

RECOMMENDATIONS

The recommended MEF-2 formula is:

	<u>Wt. %</u>
External Phase	4.0
Oleyl amine glycolate (1.0% excess acid)	0.50
Ethylene glycol (37.5%)	1.31
Water (62.5%)	2.19
JP-4	96.0

The properties which recommend the MEF-2 formula are greater ease of handling of components, small yield stress change from -40°F to 140°F, reduced corrosivity, and thermal stability.

For demulsification by shear, it is recommended that a scale-up of the jet stream vibrating reed equipment and of the membrane filter-coalescer system be investigated.

Since both demulsification systems must produce a water-free fuel, it is recommended that for both systems either a liquid cyclone or coalescer cell be investigated.

Use of the recovered fuel from either system should be investigated for direct engine use, since the amine in the fuel produces either existent or potential gum only slightly greater than specification requirements.

Since 10% to 15% of unbroken emulsion results from shear demulsification, thus presenting a disposal problem, the chemical demulsification system (ammonia, attapulgate) should be considered to recover the considerable amount of fuel represented in this residue.

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APPENDIX I. EMULSIFIER NEUTRALIZATION REQUIREMENT

Tallow amine acetate emulsifier was prepared by adding 18.9 parts (%) acetic acid to 81.1 parts of hydrogenated distilled tallow amine in EG. This ratio was also used in the MEF emulsion and was chosen because it gave the same indicated pH in isopropanol-water solution as tallow amine acetate emulsifier.

To determine if stoichiometric amounts of reactants were being used, an electrometric, nonaqueous titration was performed on the tallow amine. The amine was titrated with 0.02146N perchloric acid in acetic acid, and the combining weight was calculated. It was subsequently found that the emulsifier required only 18.1% acetic acid for stoichiometry. This means that the current emulsifier contained 5% excess acid.

Whether excess acetic acid increases, decreases, or does not affect emulsion stability had not been definitely determined. Results in Table V show that emulsion 16-1 (18.0% acetic acid) is less stable than emulsion 16 (18.9% acid).

The above electrometric, nonaqueous titration will be used to determine combining weights of other amines to be considered as replacement for the tallow amine when the combining weights are unknown.

APPENDIX II. YIELD STRESS VALUE

The revised specification for determining yield value of emulsified fuels was used in these tests. To conform to this procedure, the 50-gram cone assembly was modified to weigh 30 grams and the emulsion buoyance factor was incorporated into the calculations. Since the cone dimensions differ from those in the specification, a new graph of yield value vs. penetration (Figure 7) was prepared to correct for the dimensional difference. This chart is a plot of the following equation:

$$\text{Yield Value} = \frac{[\text{Cone Assembly Wt (grams)} - \text{Buoyance (grams)}] 980.6 \text{ dynes/gram}}{\text{Submerged Surface Area of Cone (cm}^2\text{)}} \quad (16)$$

$$= \frac{(30.0 - 0.782(0.37 + 1.047(P-1.60)[0.526(P-1.60)^2 + 1.023(P-1.60) + 0.663])) 980.6}{2.4 + 4.34[0.95(P-1.60) + 0.94][P-1.60]}$$

where P is the depth of cone penetration.

The above equation is complex, and solving it by hand to obtain the many points necessary for the drawing of subject curve was too laborious. Consequently, the IBM 1130 computer was used to calculate yield value for every five units of penetration over the desired range.

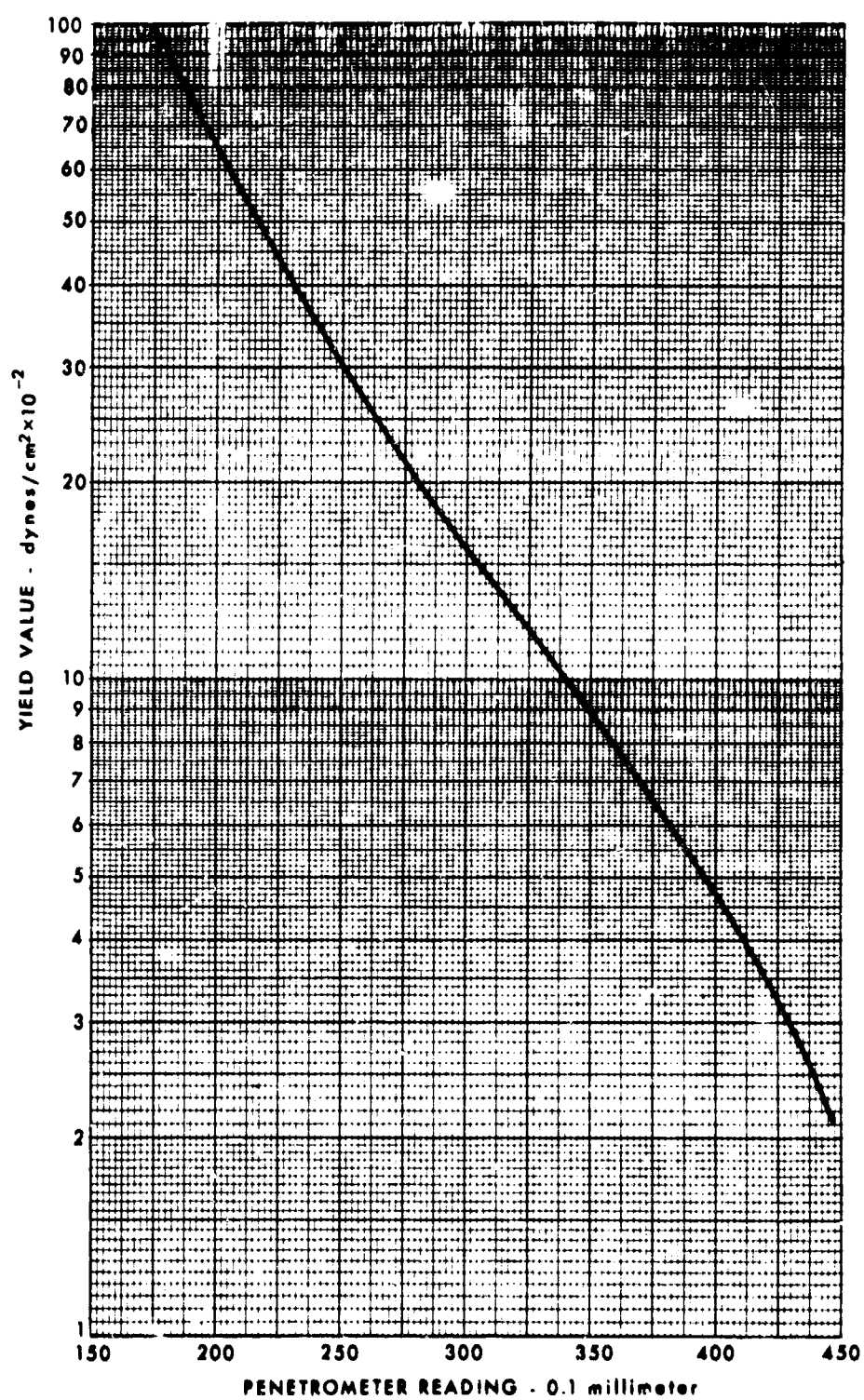


Figure 7. Yield Value vs Penetration.

APPENDIX III. PATENT COVERAGE

To protect the MEF formulation, a patent application was filed covering the MEF, MEF-1, and potential MEF-2 formulations. The application contained figures which defined the several materials parameters. Figure 8 describes the quaternary system (based upon Findlay's "The Phase Rule and Its Application," Dover Publications, New York, 1938). Apex A represents 100% liquid hydrocarbon (JP-4) or 0% external phase. Apex B represents 5% ethylene glycol; Apex C, 5% water; and Apex D, 5% emulsifier. Figure 9 is a plan view of the base BCD at the 5% plane of Figure 8. Figure 10 is the 4% plane; Figure 11, the 3% plane; and Figure 19, the 2% plane.

The pentahedron EFGHJKLM describes the most useful compositions as defined by the matrix experimentation.

The quaternary system ABCD with base BCD consists of 95-100% JP-4 mixture and 0-5% external phase. On each plane of Figures 9 through 12 at "n" % external phase, any given point represents a composition containing (100-n) % liquid JP-4 and n % external phase, where B = 5% ethylene glycol, C = 5% water, and D = 5% emulsifier. Thus, point H as an extreme has the following weight composition:

	<u>Wt. %</u>
Liquid hydrocarbon	95
External phase	5
Ethylene glycol	3.2
Water	1.1
Emulsifier	0.7
Total	100

This example expressed in our usual form would comprise an emulsion with 5% external phase, 0.7% emulsifier, and an EG/water ratio of 74.5/25.5.

Each composition represented by a point within the pentahedron EFGHJKLM, including all the points on its surface, provides a useful emulsion. As an extreme, the 2% plane of Figure 12, JKLM, defines the upper case of the pentahedron.

Emulsifiers cited comprise various long carbon chain amines neutralized with aliphatic or hydroxy aliphatic carboxylic acids. These cover tallow and cetyl amines, and acetic and hydroxy acetic acids as preferred emulsifiers.

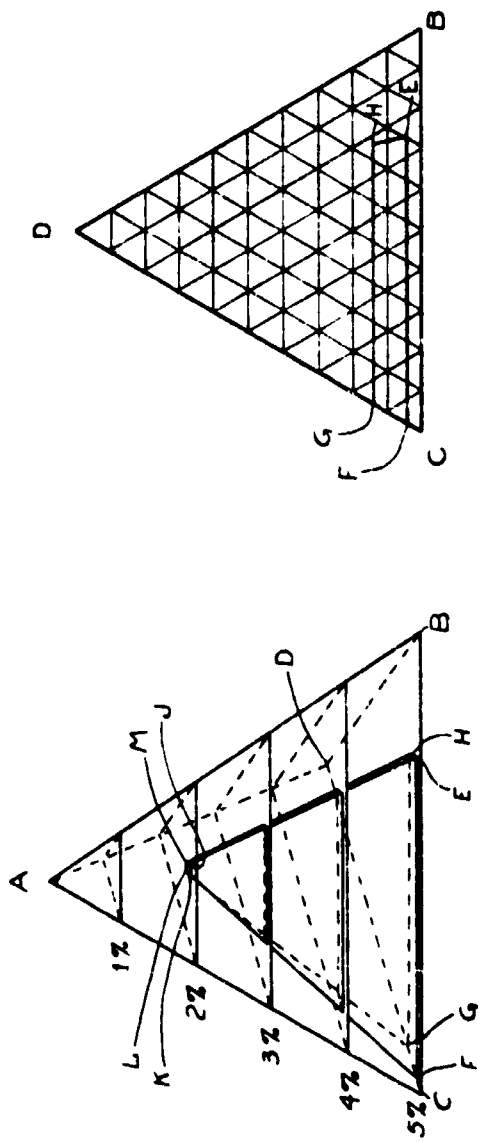


Figure 8

Figure 9

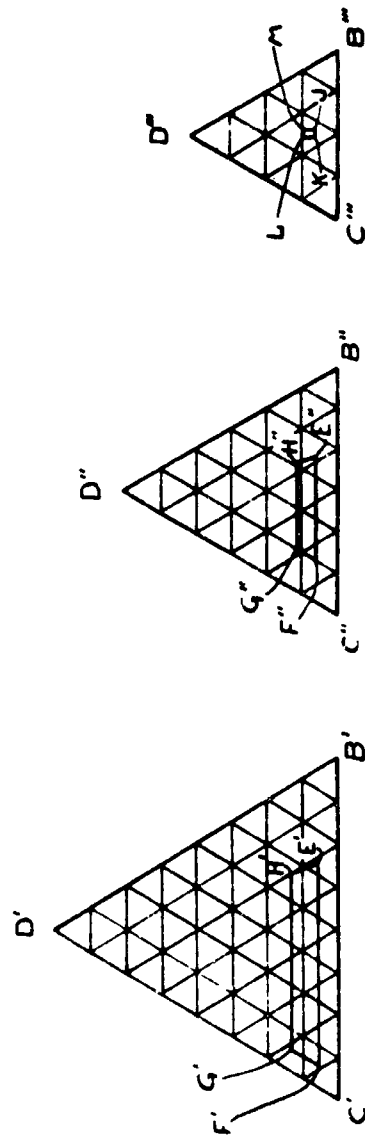


Figure 10

Figure 11

Figure 12

Preferred MEF Formulations

APPENDIX IV. THERMAL CONDUCTIVITY

SAMPLE CONTAINER OF TEST APPARATUS

The test apparatus used is shown in Figure 13. Two nickel wires of nearly identical length and diameter were held in position by a stiff lower support (A) and small upper springs (B). One wire was centered in the copper cylinder (C), and the other was placed near the circumference. The cylinder was mounted in a box surrounded by 5 inches of polyurethane foam insulation (D).

The center wire is the main temperature sensor, and the outside wire is a liquid temperature sensor used to correct for errors caused by slow temperature drift. The copper cylinder and insulator serve to stabilize the liquid temperature.

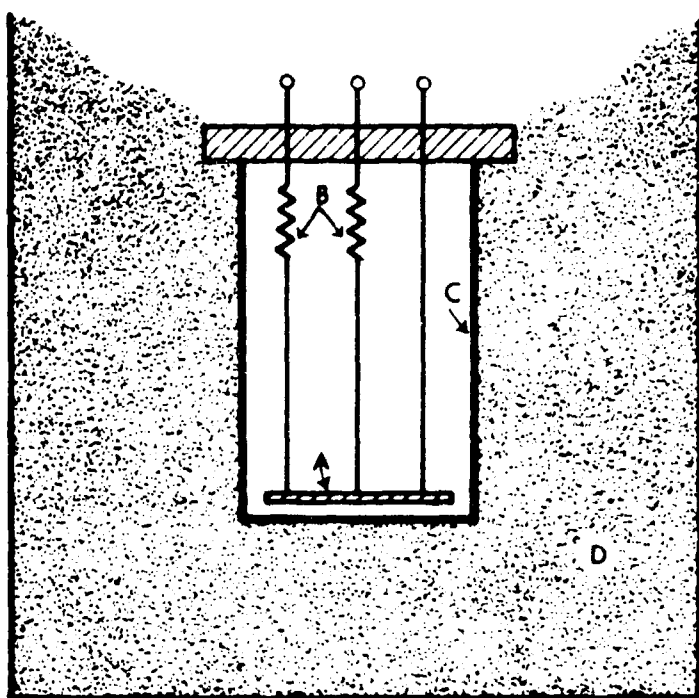
ELECTRICAL MEASURING APPARATUS

The electrical arrangement used is shown in Figure 14. R_{N2} is the center wire ($\sim 10\Omega$), and R_{N1} is the outside wire ($\sim 10\Omega$). These two along with R_R and R form a wheatstone bridge, with C_1 and C_2 capacitors used to balance out stray reactive factors. An oscillator (OSC) drives the bridge through a balanced, shielded isolation transformer (T). This transformer also matches the bridge impedance ($\sim 20\Omega$) to the oscillator (600Ω). A blocking capacitor (C_3) prevents direct current from passing through the transformer. A tuned null detector (ND) senses bridge balance, and its output is displayed on the oscilloscope, whose sweep is locked to the oscillator. In this way, off-balance direction may be determined by observing the phase of the null signal. The oscillator frequency is selected at a quiet position of the spectrum (610 Hertz was used here). The last part of the circuit is a variable-voltage DC power supply (PS) which passes current through R_{N2} by way of a 250Ω precision resistor. This current passes essentially only through R_{N2} since R_R and R are very large ($\sim 10,000\Omega$) and C_3 blocks DC. A digital voltmeter (DVM) accurately measures voltage across the 250Ω resistor; thus, the heating current ($I = V/250$) can be obtained.

Figure 15 shows all the apparatus used.

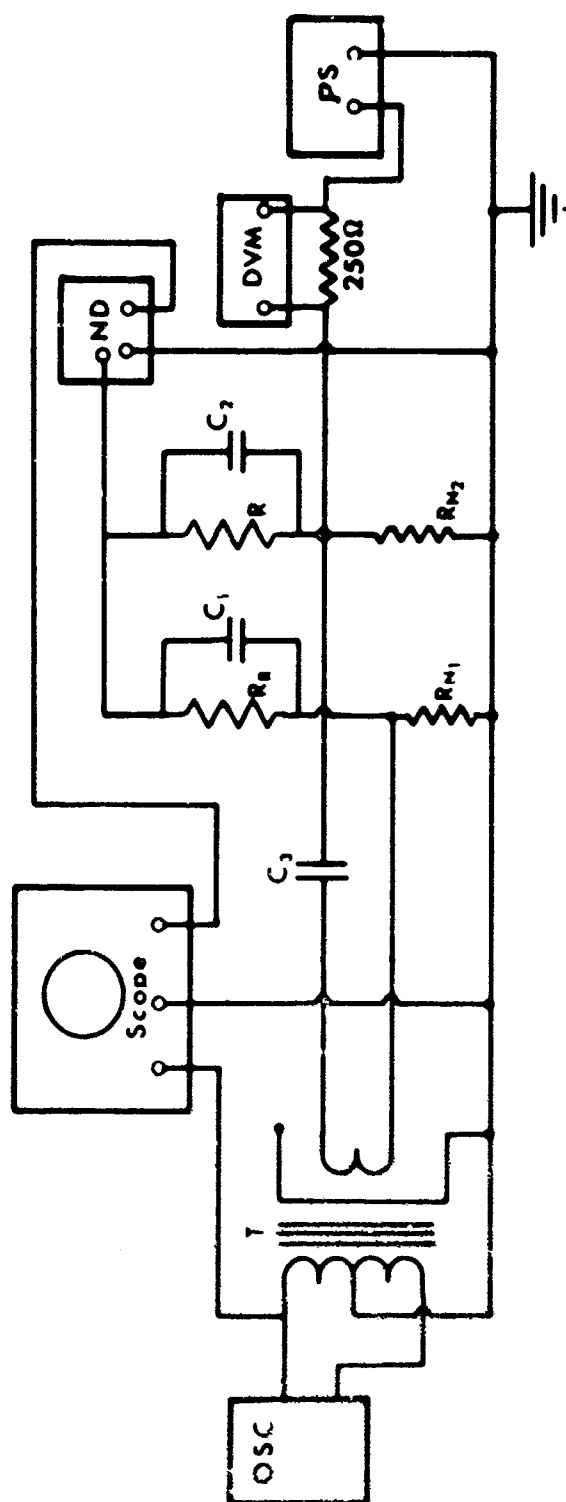
OPERATING PROCEDURE

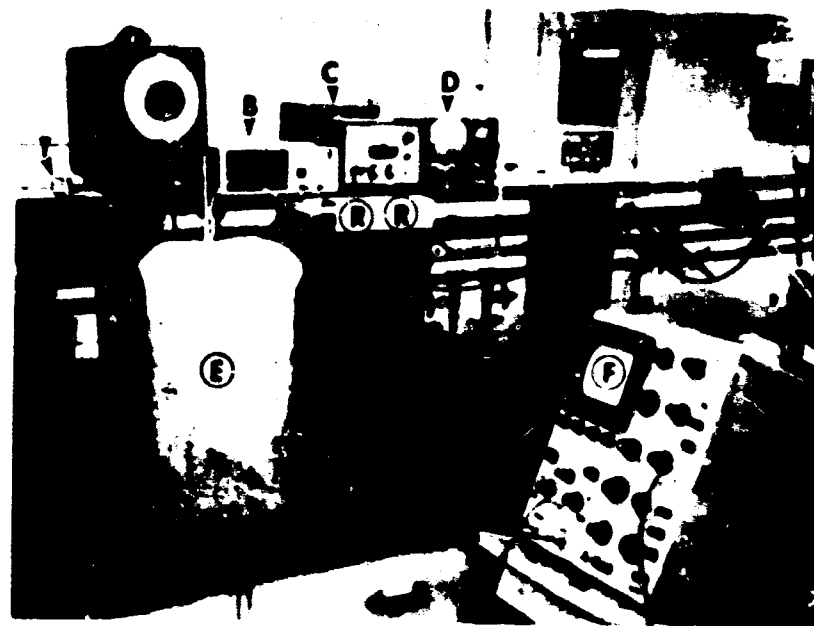
In performing the test, the sample is placed in the copper cylinder to near capacity. The detector wires are placed in



- A - Lower Support
- B - Small Springs
- C - Copper Cylinder
- D - Foam Insulation

Figure 13. Sample Container for Test Apparatus.





- | | |
|------------------------|---------------------|
| A - Oscillator | E - Sample Cylinder |
| B - Digital Volt Meter | F - Oscilloscope |
| C - Power Supply | R - Resistance |
| D - Null Detector | T - Transformer |

Figure 15. Thermal Conductivity Apparatus.

position, and a few hours are allowed for temperature equilibrium. The oscillator, null detector, and oscilloscope are turned on; balance is obtained by adjusting R_g (set near $10,000\Omega$), R , and C_2 . The oscillator output is adjusted to result in a 1:1 signal-to-noise ratio on the lowest decade of R . After balance is reasonably stable, a DC current is passed through the center wire by activating the power supply and digital voltmeter. The bridge is rebalanced and allowed to stabilize; then current and resistance readings are taken.

In practice, balance is continuously monitored by plotting R vs time every minute or two while current is set at zero or a selected value. An important point is the avoidance of convection in the liquid. This convection is controlled by making ΔT equal to 0.1°C or less and is related to resistance change by noting that the resistance coefficient of temperature corresponds to an increase of 0.07% in the resistance R , or about 7Ω . After several periods of about 10 minutes with and without various currents applied, the percentage change in $R(\Delta R/R)$ is determined and plotted vs I^2 , and the best-fitting portion of the curve is extrapolated to the origin. The inverse of the slope of this line ($I^2/\Delta R/R$) is proportional to thermal conductivity.

Table XXXV shows the experimental data. The curves used to obtain the inverse slope values listed in Table XXXV are shown in Figure 4. The calculations and values for thermal conductivity of the above fluids were discussed in Section 18.

TABLE XXXV. EXPERIMENTAL DATA - THERMAL CONDUCTIVITY

Sample	R_A (ohms)	H	R + ΔR	I (amps)	$\Delta R/R$ ($\times 10^3$)	I^2 ($\times 10^3$)	Inverse of Slope (Extrapolated)
Toluene	9950	8775.2	8779.0	0.020	4.33	4.0	
"	"	8775.0	8777.4	0.016	2.73	2.56	0.921
"	"	8775.2	8780.5	0.024	6.03	5.76	
JP-4	"	8870.2	8874.6	0.020	4.96	4.0	
"	"	8869.6	8872.8	0.016	3.60	2.56	0.758
"	"	8869.5	8876.0	0.024	7.32	5.76	
NOX-P-2	"	8772.4	8777.4	0.020	5.47	4.0	
"	"	8772.6	8775.9	0.016	3.76	2.56	0.700
"	"	8772.3	8779.5	0.024	8.20	5.76	

APPENDIX V. MICROBIAL RESISTANCE

UDRI-TM-68-07 - GROWTH AND SURVIVAL OF FUEL-UTILIZING MICROORGANISMS IN JP-4 FUEL SYSTEMS AND IN MEF-2 FUEL EMULSION SYSTEMS

A wide variety of microorganisms are capable of growing in jet fuel systems. Microbial contamination has been correlated with malfunctions of fuel system components⁴ and with corrosion of aluminum and aluminum alloys.^{5,14} Organisms growing in fuel systems can degrade a number of organic materials used as fuel tank coatings,^{8,10,12,13} and some coatings can be used as a source of nutrients for microbial growth.⁸ The predominant fuel-utilizing organisms isolated from such systems are bacteria in the genus *Pseudomonas* and fungi in the genus *Hormodendrum* (*Cladosporium*). These organisms grow abundantly in a fuel/water system with JP-4 as the sole source of carbon, producing large quantities of cells, thick mycelial mats, and precipitates.

Conversion of jet fuels to stable emulsions has been proposed to reduce flammability during transportation and storage.¹¹ In a previous study⁷ two such emulsions did not differ from nonemulsified fuel in their ability to support bacterial growth. Under some conditions, growth of a *Hormodendrum* sp. was decreased when emulsified fuel served as the carbon source.

The present study was undertaken to evaluate the effect of a third emulsion on microbial development.

Materials and Methods

Culture Media

Microbial growth was determined in both liquid and solid systems. Each system contained a mineral salts solution⁶ to which 1.5% Special Agar-Noble (Difco) was added when a solid medium was desired. The pH of the mineral solution was adjusted to 7.2 for bacteria and 5.6 for fungi prior to sterilization by autoclaving at 15 psi for 15 minutes.

MEF-2 emulsion was prepared and supplied by Monsanto Research Corporation, Dayton, Ohio. Emulsions were prepared with a Hobart mixer with oleyl amino glycolate as the emulsifying agent. Each emulsion contained 96% (w/v) JP-4 jet fuel (supplier's datum).

To prepare liquid culture systems, 40 ml of sterile salts solution was supplemented with 11 g of MEF-2 or with 15 ml of filter-sterilized JP-4 jet fuel. For solid media, 11 g of MEF-2 or 15 ml of sterile JP-4 was mixed with 40 ml of warm mineral salts agar in a sterile blade blender. The mixture was dispensed to sterile petri dishes and allowed to solidify.

Organisms

Pure cultures of *Pseudomonas aeruginosa* and *Hormodendrum* (*Cladosporium*) sp. isolated from fuel systems were used as test organisms. These organisms are stable fuel utilizers.⁹ They were maintained in a mineral-salts/JP-4 medium.

Bacterial and fungal cells were harvested by centrifugation; they were then washed three times with sterile distilled water. The aqueous suspensions were adjusted to a turbidity of 90% T in a Spectronic 20 colorimeter set at a wavelength of 550 mμ. Then 0.1 ml of bacterial cells or 1.0 ml of fungal mycelium was used to inoculate each system.

Bacterial cultures were incubated at 37°C without shaking. Bacterial growth was determined by the pour plate method using Trypticase Soy Agar (BBL). Fungal cultures were incubated at 26°C, and growth was determined qualitatively by visual observation for the presence of a mycelial mat.

Test Systems

The emulsion was tested in several ways: (1) by mixing bacterial or fungal inoculum directly with the emulsion, (2) by overlaying liquid medium with the emulsion, and (3) by mixing emulsion with mineral salts agar and preparing pour plates and streak plates. In each case, control systems were prepared by substituting JP-4 fuel for MEF-2 emulsion.

Results

Microbial growth was not detected in or on the emulsion in the absence of an aqueous (salt solution) phase.

Liquid cultures containing MEF-2 separated into three phases, while cultures containing JP-4 fuel remained in two phases. Visual inspection indicated that bacterial growth was limited to the aqueous phase, which is typical of such systems. Growth in the aqueous phases of test and control systems is summarized in Figure 16. Growth rates were the same in both systems. Both systems supported populations in excess of 10^8 viable cells per ml. Initial maximum populations were observed after

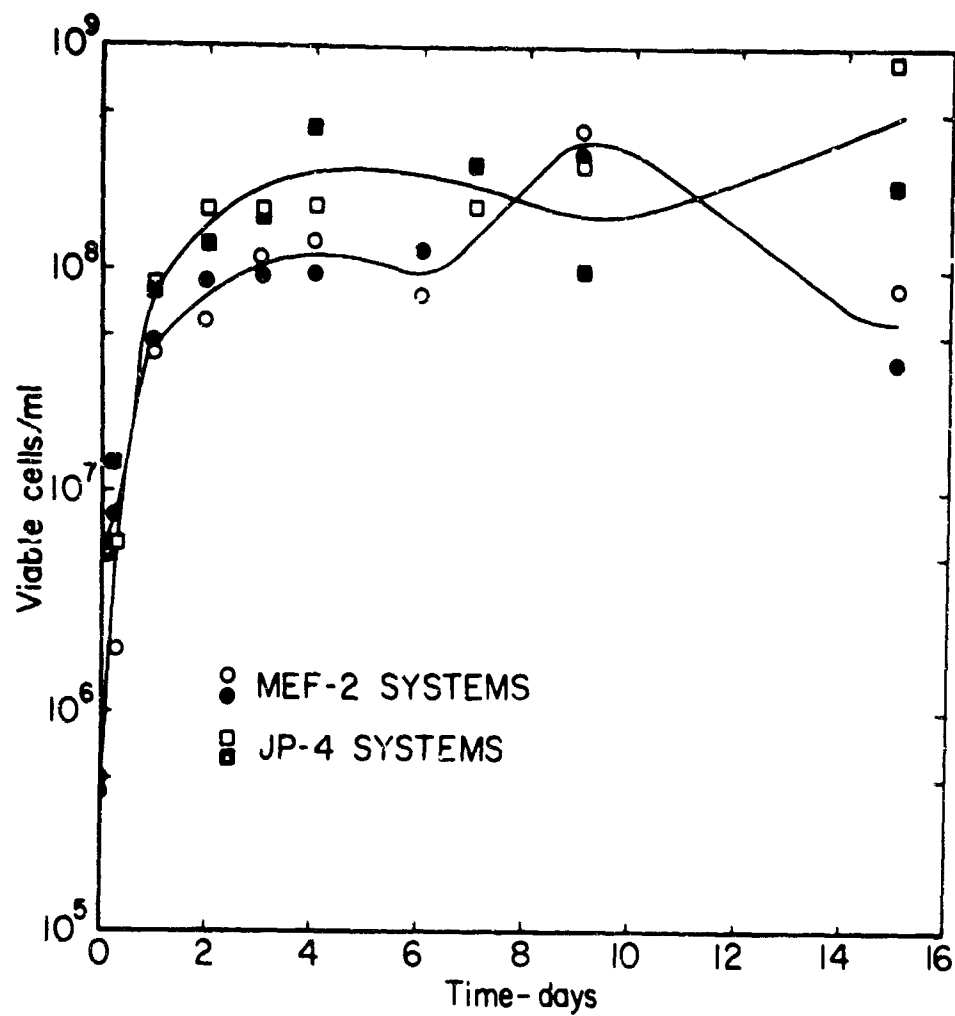


Figure 16. Growth Curves of *Pseudomonas aeruginosa* in the Aqueous Phases of Test and Control Systems.

4 days and were slightly higher in JP-4 systems than in MEF-2 systems. After 15 days' incubation, when the experiments were terminated, both systems had sizable populations, but MEF-2 systems contained fewer viable cells per ml than JP-4 systems. A thick mycelial mat of *Hormodendrum* sp. developed at the fuel/water interface in the fluid control (JP-4) system over the 30-day incubation period (Table XXXVII). Only a trace of growth was detected in the MEF-2 system. A white flocculent precipitate developed in liquid systems containing the emulsion.

No growth was observed over a 30-day period in or on a solid medium containing MEF-2 (Table XXXVIII). In a similar medium containing JP-4, mycelial development was evident though not abundant.

Discussion

The results are comparable to those obtained previously for other fuel emulsions.⁷ Microbial growth was detected only in the presence of a water phase. Fuel-utilizing organisms grew only in the aqueous phase or at the fuel/water interface.

Significant populations of *Ps. aeruginosa* developed in control (JP-4) and test (MEF-2) systems. Differences in viable counts (Figure 16) between the two systems through 10 days of incubation are not regarded as significant. MEF-2 systems contained approximately one-tenth the viable population at 15 days as found in JP-4 systems. A longer term study would be required to determine if the trend continued.

Although rate and total amount of bacterial growth did not appear to be significantly different in the emulsion system than in the nonemulsion system, it is possible that metabolic products differed due to the presence of emulsifying agent(s).

As in the case of the emulsions Alamac #1 and Alamac #2 (Reference 7), growth of the fuel-utilizing fungus was decreased in liquid MEF-2 systems. Growth was not observed in or on a solid medium containing MEF-2 as the sole carbon source. Nonemulsified JP-4 supported good growth of the fungus. These data suggest that the emulsifying agent(s) may have antifungal activity, but more critical experiments must be undertaken in this regard.

TABLE XXXVI. RESPONSE OF A <i>HORMODENDRUM</i> SP. IN FLUID CULTURES CONTAINING SALTS SOLUTION PLUS JP-4 FUEL OR MEF-2 EMULSION				
Incubation Time (days)	JP-4 Jet Fuel		MEF-2 Emulsion	
	A ^a	B	A	B
0	<u>b</u>	-	-	-
5	-	-	-	-
10	-	-	+	+
15	-	-	+	+
20	+	+	+	+
25	++	++	+	+
30	++	++	+	+
^a A and B denote replicate experiments. ^b - = no growth; + = trace of growth; + = distinct growth; ++ = good growth.				

TABLE XXXVII. GROWTH OF <i>HORMODENDRUM</i> SP. IN SOLID MEDIA INOCULATED BY THE POUR PLATE METHOD				
Time (days)	JP-4 Jet Fuel		MEF-2 Emulsion	
	A ^a	B	A	B
0	<u>b</u>	-	-	-
15	+	+	-	-
30	+	+	-	-
^a A and B denote replicate experiments. ^b - = no visible mycelium; + = trace of growth; + = no visible mycelium.				

Conclusions

MEF-2 alone did not support growth of fuel-utilizing organisms.

When MEF-2 emulsion was used as the sole organic carbon source for a fuel-utilizing bacterium in an aqueous system, it supported abundant growth. No significant differences in size of bacterial populations were noted between emulsion-cultures and cultures containing normal JP-4 fuel.

MEF-2 did not support more than a trace of growth of a fuel-utilizing fungus in the systems employed.

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<p>Optimization of the Monsanto Emulsified Fuel (MEF) was accomplished following evaluation of a 168 formulation matrix. Thermal and storage stability was best when a 1% to 2% excess of acid was used to neutralize the tallow amine. Emulsion droplet size was shown to be more a function of preparation than of thermal effect or aging. Attempts at improvement of an MEF-1 formulation from the investigation by using coupling agents or corrosion inhibitors were unsuccessful. However, change in emulsifier from tallow amine to oleyl amine markedly improved thermal stability and minimized yield stress value variation at extremes of temperature. Substitution of glycolic acid for acetic acid (the MEF-2 formula) reduced mild steel corrosion to near zero proportions and reduced cuprous metal corrosion to one-third that of the MEF formula. Evaluation of the MEF-2 formula showed that the initial viscosity decreased on storage due to loss of emulsified air and concurrently increased in density. Agitation by hand, gear, or centrifugal pump caused an increase in yield stress. Five days at 500 g's reduced the emulsifier level only 16%, and the oleyl amine glycolate was soluble in JP-4 to the extent of 0.0015-0.0018% remaining essentially in the external phase. A partial explanation for the lack of emulsion adhesion to metal surfaces is its low surface tension of about 24 dynes/cm, near that of JP-4 alone. Microbial resistance equalled that of JP-4, vapor loss was the same as that of the original MEF, and heat transfer properties were poorer than those of JP-4. Recovery of JP-4 by breaking the emulsion by mechanical shear was possible by two general techniques: pressure drop through a small orifice or passage through orifices of micron dimensions. Maximum JP-4 recovery was 90% at laboratory rates of 10 gpm using a pressure drop orifice-vibrating reed system. Further attempts to improve the effective chemical demulsification system were unsuccessful.</p>		

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Aviation Fuel Emulsions Fuel Emulsions JP-4 Emulsifiers Surfactants Safety Flammability Thermal Stability Demulsification Gas Turbine Fuel Tallow Amine Acetate Oleyl Amine Glycolate Fuel Separation Gravity Acceleration						

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